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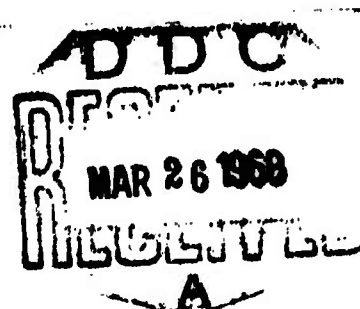
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HIGH INTENSITY LASER PROPAGATION IN THE ATMOSPHERE

Semiannual Report
1 March 1967 - 31 August 1967

TRW
SYSTEMS GROUP

HIGH INTENSITY LASER PROPAGATION
IN THE ATMOSPHERE

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INTRODUCTION AND SUMMARY

This report is concerned with two nonlinear propagation effects which limit the transmission of intense laser radiation through the atmosphere. One effect is that of self-defocusing due to heating, which can cause an undesirable decrease in the delivered power density. The defocusing results from photon absorption leading to atmospheric heating and consequently to a local decrease in the refractive index; the result is a lens effect which causes the beam to diverge. This instability is apparently significant even for exceedingly low absorption coefficients. Consequently it is necessary to have reliable information in the far wings of atmospheric absorption lines where laboratory data is meager, and where conventional pressure broadening theories are inapplicable. This report, then, presents theoretical studies on certain aspects of very-far-wing collision broadening, which are particularly pertinent to the problem of thermal defocusing in the atmosphere.

The second phenomenon studied is the stimulated Raman effect. This work represents a continuation of previous research[1] which was concerned with catastrophic beam depletion resulting from stimulated Raman scattering in the atmosphere. The new work deals with applications of the previously derived general results to an analysis of the generation and amplification of short intense pulses of Raman backscattered light.

Chapter 1 describes some preliminary theoretical studies on the far-wing collision broadening of the rotational spectrum of a polar molecule. The studies were motivated by the currently prevalent belief that a substantial part of the continuous background-absorption by the

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1. High Intensity Laser Propagation in the Atmosphere, TRW Systems Group, Final Report 05691-6003-R000, February 1967.

atmosphere in the wavelength-vicinity of 10μ is due to the very-far-wing collision broadening of the rotational spectrum of H_2O.

The basic approach of the herein described studies may be regarded as an extension of the classical Debye theory of dielectric relaxation. In this theory, the origin of dielectric absorptivity arises from the random interruption of the rotational motion of the individual molecular dipoles by impact-type collisions, i.e., collisions of <u>infinitesimal duration</u> — with other atoms or molecules of the medium. In the present work, the theory has been extended to take account of

(a) the fact that (in contrast to Debye's original assumption) the frequency of the incident light wave is large compared to rotational frequencies,

(b) quantum corrections arising from the fact that $\hbar\omega > kT$, and,

(c) the actual finiteness of time duration of collisions.

While this work was nearing completion, the authors became aware of very recent data of D. Burch on laboratory studies of $H_2O - N_2$ mixtures in the 10μ region. These studies indicated (cf. Summary of May 16, 1967 meeting on Infrared Atmospheric Absorption, page 2) that, despite the fact that the relative concentration of H_2O in the studied mixtures was $\overset{\sim}{<} 2\%$, the collisions responsible for absorption were those of H_2O molecules with each other! Such a result was found to be unexplainable within the framework of the above-described theoretical studies; moreover, the magnitude of the experimental absorption was found to be several orders larger than the theoretical prediction.

The first attempt to remove the discrepancy consisted in taking account of the shortening of the time-duration of collisions via the mechanism of attractive forces (associated with dipole-dipole interactions); as shown by the detailed expressions, such shortening would lead to an enhancement of the far-wing absorption. However, with

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physically reasonable values of the relevant molecular parameters, only marginal improvement was obtained; the calculated absorption still fell short of the experimental value by almost three orders of magnitude.

Under these circumstances, it was felt necessary to introduce some essentially new physical ingredient into the theory. One such possibility has suggested itself and is presently being pursued. Briefly, it is now felt that the origin of the far-wing absorption in H_2O vapor arises from the angular dependence of the (strong) dipole-dipole interaction. Namely, at sufficiently close — yet still accessible — distances of approach of two colliding H_2O molecules, this angular dependence provides a potential trough for the rotational motion of each molecule; within this trough, the molecules execute a type of hindered rotation — or, as it is commonly designated, a "librational" motion. The decisive point is that, according to preliminary estimates, the frequencies associated with this librational motion are substantially higher than those of free rotation — and, in fact, may be expected to encompass the 1000 cm^{-1} (10μ) region. Under these circumstances, it turns out that, according to the general theory of collision broadening, the occurrence-probability of these frequencies — in particular, those in the immediate vicinity of the external frequency — becomes the principal factor in determining the absorption. Preliminary calculations indicate that the resultant absorption far outweighs that obtained in our previous theoretical calculations.

In conclusion, then, while it is too early to be certain, the hindered-rotation mechanism looks presently rather promising.

Chapter 2 contains a discussion of pulse amplification by means of the stimulated Raman effect and of a second related topic, namely, the generation of intense, ultra-short Raman backscattered pulses recently observed in the laboratory. The first subject in Chapter 2 is the Raman amplifier which consists of a length of Raman active material through which both a beam of laser light and a beam of light at the first Stokes frequency of the laser light in the material are passing.

The beams are traveling in opposite directions and hence the second beam (the Stokes shifted beam) will be amplified by the stimulated emission of backscattered light from the first. For an input Stokes wave of arbitrary time dependence, the time dependence of the output has been formulated in terms of the solution of a differential difference equation. The solution of this equation has been reduced to quadratures for an arbitrary input, and has been obtained in closed form for the special case of a step function input.

The Raman pulse generator is a device which was first investigated by Maier, et al.[2] In their experiment a carbon disulfide cell was illuminated by a beam of intense laser light. Observations at the entrance of the cell revealed intense, short pulses of backscattered Stokes radiation. They have suggested that "A probable mechanism for the initiation of the pulse is the abrupt onset of backward stimulated Stokes emission near the exit cell surface, accompanying the occurrence of laser self-focusing in that region." As a support for their suggestion we have constructed a specific model of the influence of self-focusing on the amplification of spontaneously emitted Raman waves. This model predicts the height and shape of the emitted pulse in terms of the solution of a nonlinear differential difference equation. The equation is currently being solved by computer; it is anticipated that the analysis will be completed by the end of the present contract period.

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2. M. Maier, W. Kaiser and J.A. Giordmaine, Phys. Rev. Letters, 17, 1275 (1966).

Chapter 1.

FAR WING PRESSURE BROADENING

INTRODUCTION

This report describes some preliminary model-type theoretical studies on the far-wing broadening of the pure rotational spectrum of a polar molecule. The studies were motivated by awareness of the prevalent belief[1] that a substantial part of the continuous background-absorption in the atmosphere in the wavelength vicinity of 10μ is due to the very-far-wing broadening of pure rotation bands of H_2O with maximal intensity at wavelengths $\sim 50\mu$. As will be described more fully below, the basic approach is an extension of that employed in the corresponding problem of the far-wing broadening of near infrared vibrational lines reported previously.[2]

While this work was in progress, the authors became aware of some very recent data of D. Burch (Philco)[3] on laboratory studies of H_2O absorption in the 10μ region, which indicated that the basic broadening agency is self-broadening, i.e., H_2O - H_2O collisions. Such a result does _not_ find any natural explanation within the framework of the above-described theoretical studies; moreover, preliminary comparisons indicate that the absorption observed by Burch is almost three orders of magnitude larger than could be accounted for by these studies. A drastic modification of the theoretical approach is thus required. Such a modification has in fact suggested itself to us, but its development is presently in its very initial stage.

Under these circumstances, we feel it appropriate to devote the main body of this report to a description of the studies which have been carried out, and of their comparison with Burch's data, which reveal their inadequacy.[4] The report then concludes with a brief description of the new approach.

1. DISCUSSION OF THE MODEL

The specific model on which the calculations of this report are based may be regarded as an adaptation of the classical Debye theory of dielectric relaxation. In this theory, the collision-interrupted rotatory motion of a permanent (rigid) dipole is represented as a random walk in the dipole-orientation angle space. Collisions are considered to be instantaneous events (occurring at randomly distributed times) which, while preserving the dipole orientation, produce maximal[5] randomization of the angular velocity.

Detailed calculations within the framework of this model have, for the most part, been limited to the domain of external frequencies small compared to the natural rotational frequencies, and are hence not relevant to the present problem. The extension to higher frequencies (of the order or larger than the rotational frequencies) was carried out by E.P. Gross,[6] using an approach based on a Boltzmann equation in orientation-angle space, together with a number of different stochastic models for the elementary collision process, one of these being the above described Debye model. Instead of following this paper, the present authors have found it desirable to carry out an equivalent derivation, based on a correlation-function method.[7] This derivation is presented in Appendix I. Its crucial result is contained in equations (1.24) and (1.25), which show that for external frequencies sufficiently large compared to thermal rotational frequencies[8] the absorption probability per collision (as measured, e.g., by the imaginary part of polarizability is essentially identical to that associated with the collision-interrupted, but otherwise free motion of a fictitious charged particle whose charge, e, and mass, M, are related to the actual dipole moment, μ, and inertial moment, I, of the rotator by the formula

$$\frac{e^2}{M} = \frac{\mu^2}{I} \ . \tag{1.1}$$

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The above described correspondence is in fact not really surprising. As is by now well established by a variety of treatments on pressure broadening, the absorption intensity at a given frequency, ω, is determined by the time-variations in the electric currents on a time scale[9] $\sim \frac{1}{\omega}$ (or less). It then follows immediately that, under the condition $\omega \gg \omega_{rot}$ (postulated above), the relevant time scale is so small that, within it, the dipole, so to speak, "doesn't know that it's rotating." More prosaically, the dipolar current (in the absence of collisions) is essentially constant on a time scale $\sim 1/\omega$; the significant and meaningful current variation arises solely from collisions.

The above discussion brings us naturally to the consideration of the time-scale of the collisions themselves. In the impact-formulation of the original Debye theory (as well as in Gross' work[6] and in the appendix of the present paper), this time scale is <u>zero</u>; that is, a collision event causes an <u>instantaneous</u> alteration in the dipolar current. Such an assumption is appropriate only when the <u>actual</u> time of collision, — i.e., the time required for the angular velocity of the dipole to change — is small compared to $1/\omega$. A rough estimate of this time of collision, τ_c, is

$$\tau_c \sim \frac{\Delta r}{v} \tag{1.2}$$

where Δr is an appropriately defined range of the involved forces, and v is an appropriate velocity of traversal of the force field. In the absence of attractive forces, and for perturbers whose velocities (translational or rotational) are small compared to the rotational velocity of the dipole absorber,[10] a reasonable estimate of v is

$$v \sim (2kT/M_{red})^{1/2} \tag{1.3}$$

where M_{red} is the reduced mass for rotational motion; for e.g., H_2O itself, $M_{red} \approx 2M_H$.

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In the presence of attractive forces, (1.3) must, of course, be augmented. This modification will be discussed later. For the time being, let us assume that the interactions between the different atomic constituents of the dipole[11] and those of the perturbing molecule are primarily repulsive; as in Ref. (2) they will be represented by an expression of the form

$$V(r) = V_o e^{-\alpha r} \qquad (1.4)$$

where r is the interatomic distance between the H atom and the closest perturbing atom. Let us then carry out a numerical estimate of the validity of the basic assumption of impact theory, namely

$$1 > \omega \tau_c \sim \omega \frac{\Delta r}{v} \sim \frac{\omega}{\alpha v} \qquad , \qquad (1.5)$$

for foreign-gas broadening of H_2O at 10μ. Using the numbers,

$$\omega = 2\pi c(1000 \text{ cm}^{-1}) \approx 2 \times 10^{14} \text{ sec}^{-1}$$

$$v \approx \frac{2 \times 4 \times 10^{-14}}{2 \times 1.6 \times 10^{-24}} \approx 1.5 \times 10^5 \text{ cm/sec}$$

$$\alpha \approx 4 \times 10^8 \text{ cm}^{-1}$$

(the last being a magnitude typical[12] of exponentially repulsive forces) one obtains

$$\omega/\alpha v \approx 3$$

indicating a gross violation of the impact condition.

It is therefore proposed to carry out a calculation, somewhat analogous to that of Chapter I of Ref. 2, in which one computes the

probability that a charged particle incident on (and reflected from) a
potential barrier of the form

$$V(x) = V_o e^{-\alpha x} \qquad (1.6)$$

in the presence of an electromagnetic field of frequency, ω absorbs
(o ` emits) a quantum of energy $\hbar\omega$. As implied by the form of (1.6) the
treatment will be one-dimensional, with x representing the direction of
the line of centers of the colliding atoms (e.g., in $H_2O - N_2$ collisions
these atoms would be a hydrogen and a nitrogen atom). Of course, just
as in Chapter I of Ref. 2, such a treatment has to be augmented by an
appropriate recipe for computing effective collision diameters (which in
a one-dimensional model are actually infinite). This (rather subsidiary)
problem will be deferred for the time being.[13]

2. THE MODEL CALCULATION

In line with the discussion of the preceding section, let us consider the following problem: to solve the time-dependent Schrodinger equation

$$i\hbar \frac{\partial \psi}{\partial t} = H\psi \tag{2.1}$$

with a Hamiltonian of the form

$$H = H_o + \frac{e}{Mc} \underline{p} \cdot \underline{A} \tag{2.2}$$

$$H_o = -\frac{\hbar^2}{2M} \nabla^2 + V(x) . \tag{2.3}$$

In these expressions

$$\underline{A} = \frac{c}{i\omega} \underline{\mathcal{E}}_o e^{-i\omega+} + c.c. \tag{2.4}$$

is the vector potential associated with the external electromagnetic field (it is assumed to be "turned on" infinitely slowly, s being an infinitesimally positive number ultimately going to zero), $p = \frac{\hbar}{i} \text{grad}_{\underline{r}}$, and H_o, the field-free Hamiltonian, is given as a sum of the kinetic energy of the fictitious particle (charge, e, and mass, M, being determined according to the recipe prescribed by the Appendix Eq. I.27) and the potential energy $V(x)$ (assumed to be one-dimensional in accordance with the discussion of Section 1). In the absence of the external electromagnetic field, (2.1) has solutions of the form

$$\psi_i(r,t) = \phi_i(\underline{r}) e^{-iE_i t/\hbar} , \tag{2.5}$$

where $\phi_i(\underline{r})$ satisfies the equation

$$H_o \phi_i = E_i \phi_i . \tag{2.6}$$

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In view of the one-dimensional form of the potential, $\phi_i(\underline{r})$ is chosen to have the form

$$\phi_i(\underline{r}) = \psi_i(x) \, e^{i[k_y y + k_z z]} \tag{2.7}$$

where $\psi_i(x)$ obviously satisfies the one-dimensional equation

$$H_o^{(x)} \psi_i(x) = \left[-\frac{\hbar^2}{2M} \frac{\partial^2}{\partial x^2} + V(x) \right] \psi_i(x) = E_{ix} \, \psi_i(x) \tag{2.8}$$

with

$$E_i = E_{ix} + \frac{\hbar^2}{2M} \left(k_y^2 + k_z^2 \right) \; ; \tag{2.9}$$

it has the usual asymptotic form

$$\psi_i(x) \rightarrow \sin[k_{ix} \, x + \delta_i]. \tag{2.10}$$

Deferring for a moment the complete specification of the boundary conditions supplementary to (2.1), let us seek perturbed solutions of the form

$$\psi(\underline{r}, t) = \phi_i(\underline{r}) \, e^{-iE_i t / \hbar} + \psi_I \tag{2.11}$$

where ψ_I is proportional to the external field (and hence arbitrarily small). To obtain steady-state solutions (appropriate to the physical situation of our problem) it is desirable to write ψ_I as

$$\psi_I = e^{-iE_i t / \hbar} \left[\phi^{(+)} e^{-i\omega t} + \phi^{(-)} e^{+i\omega t} \right] e^{st} \tag{2.12}$$

where $\phi^{(+)}$ satisfies the equation[14]

$$(E_i + \hbar\omega) \, \phi^{(+)} - H_o \phi^{(+)} = \frac{e}{iM\omega} \, \underline{\mathcal{E}}_c \cdot \underline{p} \phi_i(\underline{r}) \; . \tag{2.13}$$

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Now write $\phi^{(+)}$ as

$$\phi^{(+)} = \frac{e}{iM\omega} \frac{\boldsymbol{\mathcal{E}}_o \cdot \underline{p} \, \phi_i(\underline{r})}{\hbar\omega} + \phi_{sc} \; . \tag{2.14}$$

Substituting (2.14) into (2.13), one finds that ϕ_{sc} satisfies the equation

$$(E_i + \hbar\omega)\phi_{sc} - H_o\phi_{sc} = \frac{e}{i\omega M} \frac{\boldsymbol{\mathcal{E}}_o}{\hbar\omega} \cdot [H_o\underline{p} - \underline{p}H_o]\phi_i(\underline{r}) \tag{2.15}$$

$$= \frac{e}{i\omega M} \frac{\boldsymbol{\mathcal{E}}_o}{\hbar\omega} \cdot [V\underline{p} - \underline{p}V]\phi_i(\underline{r})$$

$$= \frac{e\,\boldsymbol{\mathcal{E}}_{ox}}{\omega^2 M} \frac{\partial V(x)}{\partial x} \phi_i(\underline{r}) \tag{2.16}$$

(the elimination of all but the x-component of the external field arising from the x-dependence of the potential[15]).

It is now necessary to discuss boundary conditions. As will be discussed later these are set forth most expediently for ϕ_{sc} [i.e., as supplements to Eq. (2.16)] rather than in connection with the starting Eq. (2.1). The conditions in question turn out to be just that ϕ_{sc} represent an outgoing wave, namely

$$\phi_{sc} \xrightarrow{x \to \infty} e^{i[k_y y + k_z z]} A_{sc} \, e^{ik_{fx} x} \tag{2.17}$$

where k_{fx}, the "final" x-component of wave-vector, is determined by the equation

$$\frac{\hbar^2 k_{fx}^2}{2M} = E_{fx} = E_i + \hbar\omega - \frac{\hbar^2}{2M}\left(k_y^2 + k_z^2\right) \; . \tag{2.18}$$

Here, it will be noticed that the plane-wave y, z dependence, characteristic of $\phi_i(\underline{r})$, has been incorporated explicitly into the

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boundary conditions. In fact, at this point it is highly desirable to factor this dependence out of the problem. One achieves this simply by inserting

$$\phi_{sc} = e^{i[k_y y + k_z z]} \psi_{sc}(x) \qquad (2.19)$$

into (2.16). One obtains

$$E_{fx}\psi_{sc} - H_o^{(x)}\psi_{sc} = \frac{e\mathcal{E}_{ox}}{\omega^2 M} \frac{\partial V}{\partial x} \psi_i(x) \qquad (2.20)$$

[$H_o^{(x)}$ and $\psi_i(x)$ being defined by Eqs. (2.8) and (2.7)] whereas the boundary condition, (2.17) reduces to

$$\psi_{sc} \xrightarrow{x \to \infty} A_{sc} e^{ik_{fx}x} . \qquad (2.21)$$

With the y,z dependence now completely removed, the x-subscripts on the various constants will henceforth simply be dropped; thus

$$E_{fx}, \ E_{ix} \to E_f, E_i \qquad (2.22a)$$

$$k_{fx}, \ k_{ix} \to k_f, k_i \qquad (2.22b)$$

(it being tacitly understood that all the constants now refer to motion in the x-direction alone).

Before going on to solve for $\psi_{sc}(x)$, some brief remarks on the physical significance of the decomposition of $\phi^{(+)}$ as given by the r.h.s. of (2.14), are in order. As in analogous treatment in Ref. 2 (Chapter 1, bottom of page 11), the first term represents the amplitude for <u>virtual</u> absorption of a quantum; in particular one notes, upon inserting the asymptotic form of $\psi_i(x)$ [given by (2.7)] into (2.14), that the asymptotic behavior of the term in question pertains to a particle having a kinetic

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energy $E_i = \dfrac{\hbar^2 k_i^2}{2M}$, characteristic of the unperturbed wave. Indeed, it would even exist in the absence of any scattering potential; in fact, for a free particle its coherent superposition with the unperturbed state gives just the classical oscillatory velocity amplitude, $e \, \underline{\mathcal{E}}_o / iM\omega$.

By way of contrast, ψ_{sc} [as seen explicitly from (2.21)] describes an outgoing particle of energy $E_f = E_i + \hbar\omega$. This fact by itself is sufficient to establish it as the amplitude for the real process of quantum absorption, under consideration here; it will therefore alone be considered in what follows.

From these remarks it follows that the probability $P_{(+)}$ of an incident particle being reflected with simultaneous absorption of a quantum of electromagnetic energy is proportional to $\left| A_{sc} \right|^2$; it is in fact given by the formula[16]

$$P_{(+)} = \frac{4k_f}{k_i} \left| A_{sc} \right|^2 . \tag{2.23}$$

For the calculation of A_{sc} one proceeds as follows. One multiplies both sides of (2.20) by that solution, $\psi_f(x)$, of the homogeneous equation

$$H_o \psi_f = E_f \psi_f \tag{2.24}$$

which has the asymptotic form

$$\psi_f(x) \xrightarrow{x \to \infty} \sin(k_f x + \delta_f) \tag{2.25}$$

and integrates from minus infinity[16a] to some large value of x such that (2.21) and (2.25) are valid. One then obtains the successive equalities

$$\frac{e\mathcal{E}_{ox}}{\omega^2 M} \int_{-\infty}^{x} \frac{\partial V(x')}{\partial x'} \psi_i(x')\psi_f(x')dx' = E_f \int_{-\infty}^{x} \psi_{sc}(x')\psi_f(x')dx'$$

$$-\int_{-\infty}^{x} \psi_f(x')H_o\psi_{sc}(x')dx' = \int_{-\infty}^{x}\left[\psi_{sc}H_o\psi_f - \psi_f H_o\psi_{sc}\right]dx'$$

$$= -\frac{\hbar^2}{2M}\left[\psi_{sc}(x)\frac{d}{dx}\psi_f - \psi_f\frac{d}{dx}\psi_{sc}\right]$$

$$= -\frac{\hbar^2}{2M}\left[A_{sc} e^{ik_f x}\frac{\partial}{\partial x}\sin(k_f x + \delta_f) - \sin(k_f x + \delta_f)\frac{d}{dx}A_{sc} e^{ik_f x}\right]$$

$$= -\frac{\hbar^2 k_f}{2M}A_{sc} e^{-i\delta_f} \tag{2.26}$$

the next to the last equality holding by virtue of footnote 17 and Eqs. (2.21) and (2.25).

Combining (2.26) and (2.23), one has

$$P_{(+)} = \frac{16e^2\mathcal{E}_{ox}^2}{\hbar^4\omega^4 k_f k_i}\left|\int_0^\infty \psi_f(x)\psi_i(x)\frac{dV}{dx}dx\right|^2 \tag{2.27}$$

where the limit $x \to \infty$ has been taken in the l.h.s. of (2.26), the limit being well defined by virtue of the asymptotic behavior of the various factors in the integrand.

For unpolarized light, the standard replacement

$$\mathcal{E}_{ox}^2 \to \frac{1}{3}\mathcal{E}_o^2$$

is to be employed; (2.27) then becomes

$$P_{(+)} = \frac{16e^2\mathcal{E}_o^2}{3\hbar^4\omega^4 k_f k_i}\left|\int_0^\infty \psi_f(x)\psi_i(x)\frac{dV}{dx}dx\right|^2 . \tag{2.28}$$

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For the case of an exponentially repulsive potential

$$V = V_o e^{-\alpha x} \tag{2.29}$$

the integral on the r.h.s. of (2.28) may be evaluated explicitly. The procedure is very similar to that of Ref. 2, Chap. I, but will be given here briefly in the interests of a self-contained presentation.

The solution of

$$E\psi = H_o\psi = \left[-\frac{\hbar^2}{2M}\frac{\partial^2}{\partial x^2} + V_o e^{-\alpha x}\right]\psi \tag{2.30}$$

(for arbitrary E) with the asymptotic behavior

$$\psi(x) \xrightarrow{x \to \infty} \sin(kx + \delta) \tag{2.31}$$

is[17]

$$\psi(x) = \left[(2k/\alpha\pi)\sin\frac{2\pi k}{\alpha}\right]^{1/2} K_{2ik/\alpha}(\xi) \tag{2.32}$$

where

$$k = (2ME/\hbar^2)^{1/2} \tag{2.33}$$

$$\xi = \left(\frac{2}{\alpha}\right)\left(\frac{2MV_o}{\hbar^2}\right)^{1/2} e^{-\alpha x/2} \tag{2.34}$$

and $K_\nu(\xi)$ is the modified Bessel function of the second kind; for the case at hand, the order $\nu = \frac{2ik}{\alpha}$ is imaginary.

Inserting (2.32) and (2.33) into (2.28) one obtains, after a little algebra

$$P_{(+)} = \frac{4e^2 \mathcal{E}_o^2 \alpha^2}{3\pi^2 M^2 \omega^4} \sin\frac{2\pi k_i}{\alpha} \sin\frac{2\pi k_f}{\alpha} |\mathcal{K}|^2 \tag{2.35}$$

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where

$$\mathcal{X} \equiv \int_0^\infty K_{2ik_f/\alpha}(\xi) \, K_{2ik_i/\alpha}(\xi) \, \xi d\xi \quad . \tag{2.36}$$

As in Chapter I of Ref. 2, it is our good fortune to find the above integral in the literature.[18] The general formula (on page 334 of the quoted reference) is

$$\int_0^\infty K_\mu(ax) K_\nu(ax) x^{s-1} dx = \frac{2^{s-3} a^{-s}}{\Gamma(s)} \, \Gamma\!\left[\frac{1}{2}(s+\mu+\nu)\right] \Gamma\!\left[\frac{1}{2}(s-\mu+\nu)\right]$$

$$\times \; \Gamma\!\left[\frac{1}{2}(s+\mu-\nu)\right] \Gamma\!\left[\frac{1}{2}(s-\mu-\nu)\right] \quad ;$$

$$\mathcal{R}e \; a > 0, \mathcal{R}e \; s > |\mathcal{R}e \, \mu| + |\mathcal{R}e \, \nu| \quad . \tag{2.37}$$

Here, with $a = 1$, $s = 2$, $\mu = 2ik_f/\alpha$, $\nu = 2ik_i/\alpha$, the conditions for the validity of (2.37) are obviously fulfilled. Using also the well-known formula

$$\Gamma(1+z)\Gamma(1-z) = \frac{z\pi}{\sin\pi z} \tag{2.38}$$

one obtains, without further ado

$$\mathcal{X} = \frac{1}{2} \frac{(\pi^2/\alpha^2)(k_f^2 - k_i^2)}{\sinh\!\left[\frac{\pi}{\alpha}(k_f + k_i)\right] \sinh\!\left[\frac{\pi}{\alpha}(k_f - k_i)\right]}$$

$$= \frac{1}{2} \frac{(\pi^2/\alpha^2)(2M\omega/\hbar)}{\sinh\!\left[\frac{\pi}{\alpha}(k_f + k_i)\right] \sinh\!\left[\frac{\pi}{\alpha}(k_f - k_i)\right]}$$

$$= \frac{\pi^2}{\alpha^2} \frac{2M\omega/\hbar}{\cosh\!\left(\frac{2\pi k_f}{\alpha}\right) - \cosh\!\left(\frac{2\pi k_i}{\alpha}\right)} \quad . \tag{2.39}$$

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Substituting (2.39) into (2.35), one has

$$P_{(+)} = \frac{16\pi^2 e^2 \mathcal{E}_o^2}{3\hbar^2 \omega^2 \alpha^2} \frac{\sinh(2\pi k_i/\alpha)\sinh(2\pi k_f/\alpha)}{(\cosh 2\pi k_f/\alpha - \cosh 2\pi k_i/\alpha)^2} \ . \tag{2.40}$$

For the eventual calculation of an absorption cross-section, it is desirable to develop an expression for the net energy, ΔE_ω, which is transferred from the electromagnetic field to the charged particle.[19] To obtain ΔE_ω it would appear necessary to supplement (2.40) with an explicit expression for the alternate process of stimulated emission [i.e., to calculate $P_{(-)}$]. This, however, can be avoided by appeal to the principle of microscopic reversibility,[20] which in the case at hand, states that

$$P_{(+)}(k_i \rightarrow k_f) = P_{(-)}(k_f \rightarrow k_i) \ . \tag{2.41}$$

One now introduces this relationship into the general expression for ΔE_ω, which reads

$$\Delta E_\omega = \hbar\omega \left[\int_0^\infty dk_i I(k_i) \, P_{(+)}(k_i \rightarrow k_f) - \int_0^\infty dk_f I(k_f) P_{(-)}(k_f - k_i) \right] \tag{2.42}$$

where[21] e.g.,

$$I(k_i)dk_i = \frac{k_i dk_i \, e^{-E_i/kT}}{\int k_i dk_i \, e^{-E_i/kT}}$$

$$= \frac{dE_i}{kT} e^{-E_i/kT} \tag{2.43}$$

represents the probability that the wave vector

of the incident particle lie between k_i and $k_i + dk_i$, and where, as before, k_f and k_i are related to each other by the energy-conservation requirement

$$E_f = E_i \pm \hbar\omega \cdot \tag{2.44}$$

One then has (upon noting also from (2.44) that $k_i dk_i = k_f dk_f$)

$$\Delta E_\omega = \hbar\omega \int_0^\infty \frac{dE_i}{kT}\left(e^{-E_i/kT} - e^{-E_f/kT}\right) P_{(+)}(k_i \to k_f)$$

$$= \hbar\omega\left(1 - e^{-\hbar\omega/kT}\right) \int_0^\infty e^{-E_i/kT} P_{(+)}(k_i \to k_f) dE_i/kT \tag{2.45}$$

where, for $P_{(+)}(k_i \to k_f)$, one inserts the r.h.s. of (2.40).

The stage has now been reached where, in order to make further progress, some connection is needed between the one-dimensional treatment of this section and the actual three-dimensional situation. The analogous problem arose in Chapter I of Ref. 2 (pages 31 et seq.), and was resolved by appeal to the so-called Takayanagi approximation (for discussion and reference to Takayanagi's paper, consult Ref. 2). The principle result was that [as intimated above in footnote (19)] the rate of absorption of energy per polar molecule, W, is given by a relationship of the form

$$W = \Delta E_\omega/\tau_{eff} \tag{2.46}$$

where $1/\tau_{eff}$, the "effective" collision rate, is to be determined primarily by classical kinetic conditions, similar to (although more complicated than) those of Ref. 2. As in that case, however, for the purposes of obtaining upper estimates, it will ultimately be assumed that

$$1/\tau_{eff} \gtrsim 1/\tau \ , \tag{2.47}$$

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namely, a reliable upper bound for $1/\tau_{eff}$ is the gas-kinetic value, $1/\tau$. Values of the latter quantity are readily deduced from gas-kinetic cross-section data given in the literature.

Combining (2.46), (2.45), and (2.40), one has

$$W = \frac{16\pi^2 e^2 \mathcal{E}_o^2}{3\alpha^2} \frac{\left(1-e^{-\hbar\omega/kT}\right)}{\hbar\omega} \frac{1}{\tau_{eff}}$$

$$\times \int_o^\infty \frac{\sinh \frac{2\pi k_i}{\alpha} \sinh \frac{2\pi k_f}{\alpha} e^{-E_i/kT} dE_i/kT}{\left[\cosh \frac{2\pi k_f}{\alpha} - \cosh \frac{2\pi k_i}{\alpha}\right]^2} . \qquad (2.48)$$

The absorption cross-section, $Q(\omega)$, may now be determined simply by dividing (2.48) by the incident electromagnetic flux, $\frac{c}{4\pi} \underline{\mathcal{E}} \times \underline{\mathcal{H}} = \frac{c}{2\pi} \mathcal{E}_o^2$. One has

$$Q(\omega) = \frac{8\pi e^2}{3c\alpha^2} \left(\frac{1-e^{-\hbar\omega/kT}}{\hbar\omega}\right) \frac{1}{\tau_{eff}}$$

$$\times \int_o^\infty \frac{\sinh \frac{2\pi k_i}{\alpha} \sinh \frac{2\pi k_f}{\alpha} e^{-E_i/kT} dE_i/kT}{\left[\cosh 2\pi k_f/\alpha - \cosh 2\pi k_i/\alpha\right]^2} . \qquad (2.49)$$

From (2.49), one obtains the absorption coefficient, $\kappa(\omega)$ by the standard relation

$$\kappa(\omega) = N_a Q(\omega) \qquad (2.50)$$

where N_a is the density of absorbing molecules.

It is now of interest to discuss two special cases, (a) that for which the impact approximation is valid and (b) the more realistic situation of finite duration of collision-time.

A. Impact approximation: This is achieved most conveniently by taking the limit $\alpha \to \infty$ (i.e., zero range of interaction potential. In this case one replaces the hyperbolic functions by their lowest-order nonvanishing terms in their Taylor series, obtaining (after some algebra)

$$Q(\omega) = \frac{4e^2}{3\pi Mc\omega^2} \left(\frac{1-e^{-\hbar\omega/kT}}{\hbar\omega} \right) \int_0^\infty x^{1/2} (x+\hbar\omega/kT)^{1/2} e^{-x} dx$$

$$= \frac{4e^2}{3\pi Mc\omega^2} \left(1-e^{-\hbar\omega/kT}\right) \frac{e^{\hbar\omega/kT}}{2} K_1(\hbar\omega/2k\Gamma) \qquad (2.51)$$

(the integral being obtainable in terms of the Modified Bessel Function[22]). In the classical limit ($\hbar\omega \ll kT$) (2.51) reduces to

$$Q_{c\ell}(\omega) = \frac{4e^2}{3\pi Mc\omega^2} \qquad (2.52a)$$

which, apart from the factor 4/3, corresponds to the classical Drude expression.[23]

In the "quantum" limit, $\hbar\omega \gg kT$

$$Q_{qu} = \frac{4e^2}{3\pi Mc\omega^2} \left(\frac{\pi kT}{2\hbar\omega} \right)^{1/2} . \qquad (2.52b)$$

From the practical standpoint, the principal significance of (2.52b) is that its order of magnitude is essentially the same as that of the classical expression (2.52a) as long as $\hbar\omega/kT$ is not too large. In our case, with $\hbar\omega/kT \sim 3$, so that the magnitudes of (2.52a) and (2.52b) are comparable.

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B. Finite collision times: A useful simplification of (2.49)
which will be employed here is the replacement of the
various hyperbolic functions in the integrand by exponentials.
For the justification of this step, let us digress momen-
tarily, to list some typical magnitudes of k_i, k_f, and α.
First of all, as noted in Section I [text subsequent to
Eq. (1.51)], a representative value for α is 4×10^8 cm^{-1}.
For the k's, one proceeds from the general expression

$$k = \frac{2ME}{\hbar^2}^{1/2} = 2.3 \times 10^9 (\mathcal{M}\bar{E})^{1/2} \text{cm}^{-1} \tag{2.53}$$

where $\mathcal{M}$ is mass of the particle in units of hydrogen
atom mass and E is the energy expressed in e.v. One then
notes that, even for the extreme case of $\mathcal{M} = 1$, and for
$\bar{E} = kT \approx .025$, one has $k \approx 3.7 \times 10^8$ and, e.g.,

$$\sinh \frac{2\pi k_i}{\alpha} = \frac{1}{2} e^{2\pi k_i/\alpha} \left(1 - e^{-4\pi k_i/\alpha}\right) = \frac{1}{2} e^{2\pi k_i/\alpha} \left(1 - e^{-11}\right)$$

so that the replacement $\sinh \dfrac{2\pi k_i}{\alpha} \rightarrow \dfrac{1}{2} e^{2\pi k_i/\alpha}$

involves the negligibly small error, e^{-11}.

Introducing, then, the replacements of hyperbolic functions
by appropriate exponentials in (2.49), one has

$$Q = \frac{8\pi e^2}{3c\alpha^2} \left(\frac{1 - e^{-\hbar\omega/kT}}{\hbar\omega}\right) \frac{1}{\tau_{eff}} \int_0^\infty \frac{e^{-E_i/kT} \, dE_i/kT}{4 \sinh^2\left[\frac{\pi}{\alpha}(k_f - k_i)\right]}$$

$$= \frac{2\pi e^2}{3c\alpha^2} \left(\frac{1 - e^{-\hbar\omega/kT}}{\hbar\omega}\right) \frac{1}{\tau_{eff}} \int_0^\infty \frac{e^{-E_i/kT} \, dE_i/kT}{\sinh^2\left[\frac{2\pi\omega}{\alpha(v_f + v_i)}\right]} \tag{2.54}$$

where $v_i = (2E_i/M)^{1/2}$ and $v_f = (2/M)^{1/2}(E_i + \hbar\omega)^{1/2}$ are the velocities incident and scattered charged-particle, respectively.

One may now consider two subcases, according to whether the argument of the hyperbolic sine in (2.54) is small or large compared to unity.

(1) $\dfrac{2\pi\omega}{(v_i + v_f)} \ll 1$. In this case the hyperbolic sine is replaced by its argument and one has

$$Q = \frac{e^2}{6c\pi\omega^2}\left(\frac{1-e^{-\hbar\omega/kT}}{\hbar\omega}\right)\frac{1}{\tau_{eff}}\int_0^\infty (v_i + v_f)^2\, e^{-E_i/kT}\, dE_i/kT$$

$$= \frac{e^2}{3\pi c\omega^2}\left(\frac{1-e^{-\hbar\omega/kT}}{\hbar\omega/kT}\right)\frac{1}{\tau_{eff}}\int_0^\infty \left[x^{1/2} + (x+\hbar\omega/kT)^{1/2}\right]^2 e^{-x}\, dx$$

$$\text{(2.55)}$$

which is again an impact-type expression (somewhat similar, in fact, to the first equality of (2.51).[24]

(2) $\dfrac{2\pi\omega}{\alpha(v_i + v_f)} \gg 1$. In this case, the replacement

$$\sinh(\ \dots\ ) \to \frac{1}{2}\, e^{(\dots)}$$

is appropriate, and one has

$$Q = \frac{\pi e^2}{3c\alpha^2}\left(\frac{1-e^{-\hbar\omega/kT}}{\hbar\omega}\right)\frac{1}{\tau_{eff}}\int_0^\infty e^{-E_i/kT}\, e^{-2\pi\omega/\alpha(v_i+v_f)}\, dE_i/kT$$

which, with this introduction of a new integration variable, $y \equiv E_i/\hbar\omega$, becomes

$$Q = \frac{\pi e^2}{3c\alpha^2}\left(\frac{1-e^{-\hbar\omega/kT}}{kT}\right)\frac{1}{\tau_{eff}}\int_0^\infty e^{-bF(y)}\,dy \tag{2.56}$$

where

$$F(y) = ay + \frac{1}{y^{1/2}+(y+1)^{1/2}} \tag{2.57a}$$

$$a \equiv \frac{\alpha h}{\pi kT}\left(\frac{\hbar\omega}{2M}\right)^{1/2} \tag{2.57b}$$

and

$$b = \frac{\pi\omega}{\alpha}\left(\frac{2M}{\hbar\omega}\right)^{1/2}\,. \tag{2.57c}$$

The integral in (2.56) is evaluated in Appendix II; the result is contained in Eqs. (II.7), (II.6), and (II.8). Combining these equations with (2.56) and (2.57a,b,c), one has

$$Q = \frac{\pi e^2}{3c\alpha^2}\left(\frac{1-e^{-\hbar\omega/kT}}{kT}\right)\frac{1}{\tau_{eff}}\left(\frac{4\pi kT}{\hbar\omega}\right)\left[\frac{1}{y_s}+\frac{1}{y_s+1}+\frac{1}{y_s^{1/2}+(y_s+1)^{1/2}}\right]^{-1/2}$$

$$\exp\left\{-\frac{\hbar\omega}{kT}\left[y_s+2y_s^{1/2}(y_s+1)^{1/2}\right]\right\} \tag{2.58}$$

where (cf. Eq. II.4) of Appendix II and (2.57b), y_s is given implicitly by the relation

$$y_s^{1/2}(y_s+1)^{1/2}\left[y_s^{1/2}+(y_s+1)^{1/2}\right] = \frac{\pi kT}{\alpha h}\left(\frac{M}{2\hbar\omega}\right)^{1/2}\,. \tag{2.59}$$

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Values for a and $\bar{\nu} \equiv \omega/2\pi c$, for various values of y_s, are given in Table I.[25]

TABLE I

y_s	a	$\bar{\nu} \times 10^{-3} cm^{-1}$
.1	1.105	3.75
.15	.826	2.10
.2	.664	1.36
.25	.553	.943
.3	.476	.695
.4	.367	.415
.5	.299	.276

From this table one may find values of y_s for given $\bar{\nu}$ by e.g. graphical interpolation. It would, in fact, be desirable to carry out sufficient numerical calculations so as to obtain a plot of the absorption cross-section, Q, vs. external wave-number, $\bar{\nu}$. Due to limitations of time, this elaboration will be deferred for the final report. However, in the next section (immediately below), a numerical upper-limit estimate for Q (based on Eqs. (2.58) and (2.59)) will be carried out.

3. DISCUSSION OF RESULTS AND POSSIBLE EXTENSIONS

The first order of business in this section is the comparison of predictions of the foregoing theory for the optical absorption coefficient, i.e., with the experimental results reported by Burch.[3] Starting from the relation

$$\kappa = N_a Q \tag{3.1}$$

where N_a, the density of absorbing molecules, is related to the corresponding pressure, p_a (expressed in torr, mm. Hg) via the formula

$$N_a = 3.2 \times 10^{16} \, p_a \, cm^{-3} \tag{3.2}$$

and introducing (2.58) with $\dfrac{1}{\tau_{eff}}$ written as

$$\frac{1}{\tau_{eff}} = N_p <v> Q_{eff} \tag{3.3}$$

(with N_p, the density of perturbing molecules given by the analogue of (3.2) namely,

$$N_p = 3.2 \times 10^{16} \, p_p \, cm^{-3} \tag{3.4}$$

$<v>$ the mean relative velocity of the colliding molecules, and Q_{eff} and "effective" collision cross-section, one has

$$\kappa = Q_{eff} \, N_a \, \frac{\pi e^2 N_p}{3\alpha^2 kT} \frac{<v>}{c} \left[\frac{4kT}{\hbar\omega}\right]^{1/2} F''^{-1/2} \exp\{\ldots\} \tag{3.5}$$

where from (2.58)

$$F'' = \left[\frac{1}{y_s} + \frac{1}{y_s+1} + \frac{1}{y_s^{1/2}} \frac{1}{(y_s+1)^{1/2}}\right]^{-1/2}$$

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and the argument of exp $\{\ldots\}$ is $-\frac{\hbar\omega}{kT}\left[y_s + 2y_s^{1/2}(y_s+1)^{1/2}\right]$, y_s being given by (2.59), or Table I.

Before any numerical calculations are possible, it is necessary to determine Q_{eff} in terms of known physical parameters. Anticipating the results of the numerical calculation given below, let us bypass this problem by adopting the philosophy that we are calculating an upper bound[26] for κ. In line with this approach, we write down an upper-limit estimate for Q_{eff} by setting it equal to the gas-kinetic cross-section, Q_K. For the latter quantity, a rough estimate is provided by Laudolt-Bjornstein (6th Ed.) Vol. I, p. 369, where a value for the gas-kinetic diameter σ_T of H_2O — namely 4.59×10^{-8} cm — is quoted. Introducing this value into the formula

$$Q_K = \pi\sigma_T^2$$

(appropriate for H_2O - H_2O collisions), one has

$$Q_{eff} \leq Q_K \cong 66 \times 10^{-16} cm^2 \ . \tag{3.6}$$

Using for α the previously-cited value of $4 \times 10^8 cm^{-1}$, and $T = 300°K$ [together with formula (3.2)], one finds

$$\frac{\pi e^2 N_p}{3\alpha^2 kT} \cong 1.2 \times 10^{-6} p_p . \tag{3.7a}$$

Taking for the mean relative velocity of H_2O - H_2O collisions the relation[27]

$$<v> = \sqrt{2}\left(\frac{2kT}{M_{H_2O}}\right)^{1/2} = .76 \times 10^5 cm/sec.$$

one has

$$\frac{<v>}{c} = 2.5 \times 10^{-6} \ . \tag{3.7b}$$

In proceeding further, it is convenient to choose for the external wave number the value $\bar{\nu} = 934$ cm^{-1}, which corresponds (cf. Table I) to $y_s = .25$ and $a = .553$ (and is nevertheless sufficiently close to 10^3cm^{-1}). One then has

$$\left(\frac{4\pi kT}{\hbar\omega}\right)^{1/2} = 1.78 \tag{3.7c}$$

$$\left[F''\right]^{-1/2} = .390 . \tag{3.7d}$$

Inserting these results [together with (3.4) and (3.6) into (3.5)], one finds

$$\kappa \; \gtrsim \; 4.4 \times 10^{-10} \, p_o p_p \exp\{....\} . \tag{3.8}$$

Turning now to the experimental results, Burch concluded that in an atmosphere-like environment with a H_2O-vapor pressure of 15 torr (mm Hg), self-broadening (i.e., H_2O - H_2O collisions) constitutes the main absorption agent. In line with this conclusion, let us therefore insert

$$p_a = p_p = 15 \text{ torr}$$

into (3.8), thereby obtaining

$$\kappa \; \gtrsim \; 10^{-7} \exp\{....\} . \tag{3.9}$$

Deferring for the moment the numerical evaluation of exponential factor, we note that, under the cited conditions, Burch obtains .88 transmission of 10 micron light through a path of 1 km; this corresponds to an absorption coefficient

$$\kappa_{ex} = -10^{-5} \log .88 \; \cong \; 1.3 \times 10^{-6} \text{cm}^{-1} \tag{3.10a}$$

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which is one order of magnitude larger than the pre-exponential factor in (3.9).

Turning finally to the exponential factor, one finds [from the expression for its argument given in the text immediately subsequent to (3.5)] that (with $\hbar\omega/kT = 2\pi\hbar c\bar{\nu}/kT = 3.98$)

$$\exp\{....\} = \exp\{-(3.98)(1.37)\} = \exp\{-5.45\} = .43\text{x}10^{-2}. \quad (3.10\text{b})$$

It is thus seen that the theoretical value of κ is smaller than κ_{exp} by at least three orders of magnitude!

In seeking a road out of this impasse, one should note that the primary "culprit" is the exponential factor, accounting, as it does, for two out of the three orders of magnitude of discrepancy. Physically, this factor represents the effect of finiteness of collision time τ_c — in particular the fact that τ_c is so large that the condition for the validity of impact-type theory (namely, $\omega\tau_c < 1$) is grossly violated.

In this connection, it may be helpful to recall the remarks of the second paragraph of Chapter I of Ref. 2 (albeit somewhat rephrased for application to the present problem). Three alternative physical regimes were therein described.

1. The domain of external frequencies obeying the condition[28] $\omega\tau_c < 1$: This is the regime of the impact theory.

2. For frequencies such that $\omega\tau_c > 1$, the spectral profile will follow the predictions of the so-called statistical theory. In this theory, one focuses attention on the collision-induced perturbation of the instantaneous transition frequency.[29] Two possibilities arise. If a collision gives rise to perturbation of the system (during the transient existence of the collision complex $H_2O - H_2O$), such that a perturbed transition frequency

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momentarily coincides with the external frequency, ω, the spectral intensity, $I(\omega)$, will be proportional to the occurrence-probability of such a perturbation — i.e., the probability that any one of the perturbed (rotational) transition frequencies lie within a unit differential frequency range about the spectral frequency, ω.

3. If, on the other hand, there are no collisions which give rise to perturbed transition frequencies in the vicinity of the spectral frequency, ω, one may expect the spectral intensity, $I(\omega)$, to decrease exponentially with increasing frequency-discrepancy (said frequency-discrepancy being the difference between ω and the closest perturbed (rotational) transition frequency).

With respect to the theory of Section II of this paper, we have already seen that, under the given physical situation of interest to us, the condition $\omega\tau_c < 1$ does not apply, so that the impact-type frequency distribution (case 1) does not occur.

As far as the second of the above-listed three cases is concerned — the theory contains no effective mechanism for rotational perturbations of the magnitude required to encompass frequencies in the domain of interest (10^3cm^{-1}). The frequency variation of the absorption coefficient therefore falls into the third category — as is in fact evidenced by the appearance of the exponential factor on the r.h.s. of Eq. (3.5) (the negative argument of which is readily shown from Eq. (2.58) and Table I to be a numerically increasing function of frequency).

At this point a qualifying remark is in order. In a strict mathematical sense the change in rotational motion which arises via interaction of the rotating dipole with the (assumed exponentially repulsive) potential of the colliding particle — taking place as it does in a finite time, τ_c — is characterized by a frequency-occurrence distribution

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which certainly includes the spectral frequency of interest ($\bar{\nu} = 10^3 \text{cm}^{-1}$) (otherwise the absorption coefficient at that frequency would be zero). In fact, from this strictly mathematical point of view, there is no distinction between cases 2 and 3. However, especially under the conditions $\omega\tau_c \gg 1$, it is, in the opinion of the present author, physically meaningful to ask whether, within some sub-interval of the collision time, τ_c, the rotational motion may be characterized, at least momentarily, by a frequency in the vicinity of 10^3cm^{-1}. Such a possibility will in fact be suggested at the end of this section; although detailed calculations have not been performed, it is (hopefully) anticipated that the suggestion will provide the key to the understanding of Burch's experimental findings.

However, to proceed systematically, let us first investigate one other possibility of increasing the absorption cross-section — a possibility suggested by comparison of (2.58) with the previously obtained impact expression (2.55). Such comparison — taken in conjunction with the text immediately subsequent to Eq. (3.10) — immediately poses the question as to whether some mechanism can be found to diminish the argument of the hyperbolic sine in Eq. (2.54) to the point where sub-case 1 of the previous section obtains, i.e., where

$$\frac{2\pi\omega}{\alpha(v_i + v_f)} \;\lesssim\; 1 \;. \tag{3.11}$$

Such a mechanism is, at least in principal, provided by the existence of attractive interactions; the question as to whether it is actually adequate will now be studied.

In order to simplify the discussion, let us introduce the approximation of considering the attractive interaction, $V_a(x)$ (which, in practice would vary as some inverse power of x_1) to be constant, $-V_a$, — equal in magnitude to its value at the classical turning point.[30]

Just as in the somewhat analogous Takayanagi approximation, discussed in Ref. (2), (Chapter I, p. 31-32), this approximation should be valid — at least for semiquantitative estimates — when $V_a(x)$ varies sufficiently slowly so that

$$k_i \left| \frac{d}{dx} \log V_a(x) \right| > 1 \qquad (3.12a)$$

$$k_f \left| \frac{d}{dx} \log V_a(x) \right| > 1 . \qquad (3.12b)$$

Since this condition is already on the borderline of being obeyed by the relatively rapidly varying repulsive potential, it will here be assumed to be applicable without further ado.

With the assumption of constant attractive potential the analysis becomes rather simple, in that the velocities v_i and v_f in (2.54) are now given by the formulae

$$v_i = (2/M)^{1/2} (E_i + V_a)^{1/2} \qquad (3.13a)$$

$$v_f = (2/M)^{1/2} (E_i + V_a + \hbar\omega)^{1/2} , \qquad (3.13b)$$

with E_i retaining its former significance as the initial energy [31] at $x \to \infty$.

Introducing (3.13a) and (3.13b) into Eq. (2.54) — together with the additional assumption (to be verified below) that for the case of interest V_a is sufficiently larger than E_i to permit us to neglect the latter quantity in (3.13a) and (3.13b), the integral in (2.54) is immediately evalued, and one obtains

$$Q = \frac{2\pi e^2}{3e\alpha^2} \left(\frac{1-e^{-\hbar\omega/kt}}{\hbar\omega} \right) \frac{1}{\tau_{eff}} \operatorname{csch}^2 \left\{ \frac{2\pi\omega/\alpha}{(2/M)^{1/2} \left[V_a^{1/2} + (V_a + \hbar\omega)^{1/2} \right]} \right\} . \qquad (3.14)$$

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One sees that, provided that V_a is sufficiently large — i.e., large enough so that the condition

$$\frac{2\pi\omega/\alpha}{(2/M)^{1/2}\left[V_a^{1/2}+(V_a+\hbar\omega)^{1/2}\right]} < 1 \qquad (3.15)$$

is obeyed, impact-type behavior will result, with Q being given by[32]

$$Q = \frac{e^2}{3\pi M\omega^2 c}\;\frac{1-e^{-\hbar\omega/kT}}{\hbar\omega}\;\frac{\left[V_a^{1/2}+(V_a^{1/2}+\hbar\omega)\right]^2}{\tau_{eff}} \quad . \qquad (3.16)$$

If, on the other hand, (3.15) is not fulfilled, (3.14) becomes

$$Q \cong \frac{2\pi e^2}{3c\alpha^2}\left(\frac{1-e^{-\hbar\omega/kT}}{\hbar\omega}\right)\frac{4}{\tau_{eff}}\exp\left\{-\frac{4\pi\omega/\alpha}{(2/M)^{1/2}\left[V_a^{1/2}+(V_a+\hbar\omega)^{1/2}\right]}\right\} \cdot \qquad (3.17)$$

In order to proceed further it is now necessary to put numbers into (3.15). Inserting values for the physical quantities which have already been employed, viz:

$$\alpha = 4 \times 10^8 \text{ cm}^{-1}$$

$$\bar{v} = 934 \text{ cm}^{-1}$$

and

$$M = 2\,M_H$$

into (3.15), one obtains

$$V_a + (V_a + \hbar\omega)^{1/2} > 2.9 \text{ ev} \quad . \qquad (3.18)$$

The required value of V_a is then seen to be $\sim (2.9)^2 = 8.4$ e.v. Such a magnitude is impossibly large.

A reasonable estimate of the magnitude of V_a to be expected in H_2O-H_2O collisions may be obtained by using force-constant data derived from experimental values of the virial coefficient in H_2O vapor. A fairly exhaustive discussion of various representations of the interaction-potential between two water molecules — with associated numerical values — is contained in the book, <u>Molecular Theory of Gases and Liquids</u> by Hirschfelder, Curtiss, and Bird (HCB). For our purposes, one of the simpler forms, the so-called Stockmayer potential [HCB, page 211, Eq. (1.3-33)],

$$V = 4\varepsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right] + \left[\frac{\underline{\mu}_1 \cdot \underline{\mu}_2}{r^3} - \frac{3(\underline{\mu}_1 \cdot \underline{r})(\underline{\mu}_2 \cdot \underline{r})}{r^5} \right]$$

$$= 4\varepsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right] - \frac{\mu^2}{r^3} \left[2\cos\theta_1 \cos\theta_2 + \sin\theta_1 \sin\theta_2 \cos(\phi_2 - \phi_1) \right] \quad (3.19)$$

will be employed. In this form, the interaction between two identical polar molecules is expressed as a sum of a Lennard-Jones potential (r=intermolecular distance) and a dipole-dipole term, in which the charge distributions of the individual molecules are represented as point dipoles (θ_1, ϕ, and θ_2, ϕ_2 being the polar coordinates of the dipoles with polar axis parallel to the intermolecular vector, r). The values of the constants ε, and σ for the H_2O-H_2O interaction are listed in Table (3.10-1) (page 216 of HCB). They are

$$\varepsilon/k = 380°K \quad (3.20a)$$

$$\sigma = 2.65A \quad (3.20b)$$

which, together with the known dipole moment

$$\mu_{H_2O} = 1.84 \times 10^{-18} \text{ e.s.u.} \qquad (3.20c)$$

provides us with a concrete expression for $V(\underline{r})$.

The procedure to be used here for obtaining an upper estimate for V_a from (3.19) is as follows. One maximizes the attractive interactions by taking the dipole moments $\underline{\mu}_1$ and $\underline{\mu}_2$ both parallel to the intermolecular separations (i.e., $\theta_1 = \theta_2 = 0$), (3.19) thereby reducing to

$$V = 4\varepsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right] - \frac{2\mu^2}{r^3} . \qquad (3.20)$$

One then identifies V_a with the values of $\alpha\mu^2/r^3$, where r_o is the closest distance of approach of the two molecules. An approximate condition for the determination of r_o is[33]

$$V(r_o) = 0 \qquad (3.21)$$

which with the introduction of a new variable

$$x_o = (\sigma/r_o) \qquad (3.22)$$

gives

$$0 = V(x_o) = 4\varepsilon \left\{ x_o^4 - x_o^2 - \frac{\mu^2}{2\sigma^3\varepsilon} x_o \right\} . \qquad (3.23)$$

Discarding the trivial solution, $x_o = \infty$, one has then to solve the cubic equation

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$$x_o^3 - x_o = \frac{\mu^2}{2\sigma^3 \epsilon} \quad . \tag{3.24}$$

From (3.20a), (3.20b), (3.20c), one determines the numerical value of the constant term in (3.24) to be

$$\frac{\mu^2}{2\sigma^3 \epsilon} \quad . \tag{3.25}$$

A sufficiently accurate solution of (3.24) and (3.25) is

$$x_o = 1.48 \tag{3.26}$$

which, when substituted into the last term of (3.23), gives

$$V_a^{(max)} = \frac{2\mu^2}{r^3} = \frac{2\mu^2}{\sigma^3} x_o = 5.4 \times 10^{-13} \text{ erg} = .34 \text{ ev} \quad . \tag{3.27}$$

Comparing (3.27) with the value of V_a required to satisfy (3.18) — namely $V_a \overset{\sim}{>} 8.4$ ev — one sees that (3.17), rather than the impact expression, (3.16), is the appropriate formula for Q. Let us therefore combine (3.16) with (3.1) and (3.3) to obtain the following expression for the absorption coefficient

$$\kappa = Q_{eff} \, N_a \, \frac{8\pi e^2}{3\alpha^2} \left(\frac{1-e^{-\hbar\omega kT}}{\hbar\omega} \right) \frac{\langle v \rangle}{c} \exp \left\{ - \frac{4\pi\omega/\alpha}{(2/M)^{1/2} \left[V_a^{1/2} + (V_a + \hbar\omega)^{1/2} \right]} \right\} \quad . \tag{3.28}$$

Upon inserting the numbers given by (3.21), (3.7a), (3.6), (3.7b) and

(3.27) into (3.28), and utilizing the (appropriate) formula $M = 2M_H$, as well as $\alpha = 4 \times 10^{10}$ cm^{-1}, $\bar{v} = 943$ cm^{-1}, and $T = 300$ K, one has (with the neglect of $e^{-\hbar\omega/kT}$,

$$\kappa \leq 1.06 \times 10^{-9} \, p_a p_p \exp\left\{-4.6\right\} \text{ cm}^{-1} \tag{3.29a}$$

$$= 2.5 \times 10^{-7} \exp\left\{-4.6\right\} \text{ cm}^{-1}$$

(the last number being obtained from $p_a = p_p = 15$ torr, in conformance with Burch's experimental conditions). Finally, with $\ell^{-4.6} = .01$, one has

$$\kappa = 2.5 \times 10^{-9} \text{ cm}^{-1} \tag{3.29b}$$

which exceeds the previous upper limit estimate, given by (3.9) and (3.10), by a factor of $2.5/.43 = 5.8$, but still falls short of the experimental number, given by (3.10), by a factor

$$\kappa_{ex}/\kappa_{th} > 520 \tag{3.30}$$

i.e., still close to three orders of magnitude! It thus appears that a substantially new physical ingredient has to be injected into the theory. In what follows, one such possibility, which appears to be hopeful, will be discussed briefly.[34]

The new physical ingredient is in fact contained in Eq. (3.19) — namely, in its dependence on the angular orientations of the dipoles (as given by the second term). Preliminary estimates indicate that, at intermolecular distances of the order of $r_o = \sigma/x_o^{1/3} \approx 2.2$A (as given by (3.26) and (3.20b)), the rotational motion is sufficiently hindered so as to be converted into libration about the potential minimum ($\theta_1 = \theta_2 = 0$). According to (rather crude) preliminary estimates, the

associated librational frequencies are in a domain $\sim$ 500 cm^{-1}. In view of the fact that, at the distance of closest approach the dipole-dipole approximation is certainly inaccurate for quantitative estimates of librational frequencies,[35] this estimate should, in the opinion of the present authors, be regarded as promising.

In this connection, some remarks concerning the absorption spectrum of H_2O in its condensed phases are in order. It is known[36] that whereas the vibrational spectrum of H_2O vapor is largely retained in both water and ice (with relatively small frequency shifts), the rotational spectrum is wiped out. In its place, there appears a broad absorption band, whose maximum varies from 700 cm^{-1} (liquid) to 850 cm^{-1} (ice at $-9°C$). This band, usually designated as a "librational" band, is considered from hindered rotational motion — the latter being associated with H-bond formation. The H-bond in turn is generally considered to owe its existence to the primarily electrostatic attraction between one of the (positively-charged) H-atoms of a given H_2O molecule and the (negatively-charged) O-atom of a neighboring H_2O molecule.

Apart from quantitative detail, this picture is essentially identical to that suggested in this section. Namely, even in the gas phase, at sufficiently close distances of approach of two colliding H_2O molecules, a temporary dimer $(H_2O)_2$ is formed; it is eminently reasonable that, during its (admittedly momentary) existence, this dimer possesses librational (hindered-rotational) frequencies in the spectral range of interest $(10^3 cm^{-1})$. The principal problem is then to compute the occurrence-probability of a unit frequency range about an arbitrary spectral frequency; according to the statistical theory of collision broadening[37] a knowledge of this occurrence-probability will lead directly to the absorption coefficient for said spectral frequency.

In this appendix, the relationship between the real problem of absorption associated with the collision-interrupted motion of a rotating dipole and the text-model of absorption by a charged particle undergoing collisions with fixed scattering centers will be developed.

The basic starting point of the treatment is the Kramers-Heisenberg formula for the polarizability, α, of a (rigid) rotating dipole, interacting with a fixed (random) array of scattering centers (generalized to include the dissipative and finite temperature effects). This expression reads

$$\alpha = - \frac{1}{Z} \sum_{nm} e^{-\beta E_n} \left| <n|\mu_z|m> \right|^2 \left[\frac{1}{E_n - E_m + \hbar\omega + i\hbar s} \right. $$

$$\left. + \frac{1}{E_n - E_m - \hbar\omega - i\hbar s} \right]. \tag{I.1}$$

Here $\beta = 1/kT$ (with k and T respectively Boltzmann's constant and absolute temperature), Z is the partition function of the system E_n is any one of the (exact) eigen-energies of the total system, $<n|\mu_z|m>$ is a typical matrix element of e.g., the z-component[38] of the dipole moment, ω is the external frequency and s an infinitesimal positive number.[39]

Of specific interest here is the imaginary component of polarizability, α_i. This quantity is gotten by taking the imaginary part of the r.h.s. of (I.1); with the aid of the standard relationship

$$\lim_{s \to 0} \text{Im} \frac{1}{x \pm is} = \mp \pi\delta(x)$$

it takes the form

$$\alpha_1 = \frac{\pi}{Z} \sum_{nm} e^{-\beta E_n} \left| <n|\mu_z|m> \right|^2 \left[\delta(E_n - E_m + \hbar\omega) - \delta(E_n - E_m - \hbar\omega) \right]$$

$$= \frac{\pi}{Z} \sum_{nm} (e^{-\beta E_n} - e^{-\beta E_m}) \left| <n|\mu_z|m> \right|^2 \delta(E_n - E_m + \hbar\omega)$$

$$= \frac{\pi}{Z} \frac{1 - e^{-\beta\hbar\omega}}{1 + e^{-\beta\hbar\omega}} \sum_{nm} (e^{-\beta E_n} + e^{-\beta E_m}) \left| <n|\mu_z|m> \right|^2 \delta(E_n - E_m + \hbar\omega)$$

$$= \frac{\pi}{Z} \tanh \frac{\beta\hbar\omega}{2} \sum_{nm} e^{-\beta E_n} \left| <n|\mu_z|m> \right|^2 \left[\delta(E_n - E_m + \hbar\omega) + \delta(E_n - E_m - \hbar\omega) \right] \qquad (I.2)$$

wherein the device of summation-index interchange has been utilized repeatedly, and where cognizance has been taken of the relationship

$$E_m = E_n + \hbar\omega$$

in writing the third equality.

One now expediently introduces the Dirichlet representation

$$\delta(x) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{ixt} \, dt$$

for the delta function into (I.2); the standard rules of matrix multiplication may then be utilized to rewrite (I.2) as

$$\alpha_1 = \frac{1}{\hbar} \tanh \frac{\beta\hbar\omega}{2} \int_{-\infty}^{+\infty} \cos \omega t <\mu_z(t)\mu_z(o)> \, dt \qquad (I.3)$$

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where

$$\langle \mu_z(t)\mu_z(o)\rangle \equiv \frac{1}{Z} \text{Tr} \left\{ e^{-\beta H} e^{iHt/\hbar} \mu_z e^{-iHt/\hbar} \mu_z \right\} \qquad (I.4)$$

is the dipole-dipole "response" function, H being the Hamiltonian operator of the total system.

In this appendix, the discussion will be restricted to classical conditions — specfically[40]

$$\hbar\omega < kT \qquad (I.5a)$$

$$\hbar\omega_{\text{rotational}} < kT \qquad (I.5b)$$

(I.3) may then be approximated by

$$\alpha_i = \frac{\beta\omega}{2} \int_{-\infty}^{+\infty} \cos \omega t \langle \mu_z(t)\mu_z(o)\rangle \, dt . \qquad (I.6)$$

In order to proceed further, specific assumptions concerning the dynamics of the system have to be introduced. In this treatment, said dynamics will be described by a stochastic model, of the general type developed in the theory of Brownian motion. Specifically, it will be assumed that

(a) in the absence of collisions, the dipole undergoes simple rotatory motion (characteristic e.g., of a simple rigid-rotator possessing no internal angular momentum) and

(b) at certain "impact" times, t_i, the vector angular velocity, $\underline{\omega}_i$, changes abruptly to a new value, $\underline{\omega}_{i+1}$; however, the

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orientation of the dipole, μ_i/μ, remains unchanged.[41] It
is further assumed that the direction of $\underline{\omega}_{i+1}$, apart from
being perpendicular to the rotator-axis (and hence to $\underline{\mu}_i$) is
otherwise randomly arbitrary.

On the basis of this model, the calculation of the response function
$\langle \mu_z(t)\, \mu_z(o) \rangle$ may be carried out as follows. In the time interval be-
tween zero and t (here considered positive for the sake of definiteness;
later, it will be established that the response function is an even
function of t) there will in general occur a certain number of impacts at
times t_1, t_2, ... t_{n-1}; in each of the n intervals in-between collisions,
the motion is that of pure rotation. Denoting by $\underline{\mu}_i$ the value of $\underline{\mu}$ at
the ith collision time, t_i, one has

$$\underline{\mu}(t) = \underline{\mu}_i \cos \omega_i \ (t-t_i) = \frac{\underline{\omega}_{i+1} \times \underline{\mu}_i}{\omega_{i+1}} \ \sin \omega_i \ (t-t_i) \ .$$

Using the above stated assumption concerning randomness of
direction of the angular-velocity vector, $\underline{\omega}_{i+1}$, in a plane perpendicular
to $\underline{\mu}_i$, one has immediately[42] (upon replacing i by i-1 for convenience)

$$\langle \underline{\mu}(t') \rangle = \langle \underline{\mu}_{i-1} \rangle \langle \cos \omega_i (t'-t) \rangle ; \ (t_{i-1} \leq t \leq t_i; \ t_o = 0). \quad (I.7)$$

In particular

$$\langle \underline{\mu}_i \rangle = \langle \underline{\mu}_{i-1} \rangle \langle \cos \omega_i \ (t_i - t_{i-1}) \rangle = \langle \underline{\mu}_{i-1} \cos \omega_i \ \theta_i \rangle$$

where $\theta_i = t_i - t_{i-1}$ is the time interval between the i'th and the $(i-1)^{i'th}$
collision; the various θ_i are assumed to be distributed according to the
standard relationship

$$W(\theta_i)d\theta_i = e^{-\theta_i} d\theta_i / \tau \quad . \tag{I.8}$$

For the final interval between the times of last impact, t_{n-1} and time t, one has

$$\langle \underline{\mu}(t) \rangle = \langle \underline{\mu}_{n-1} \rangle \langle \cos \omega_n \theta_n \rangle \tag{I.9}$$

with $\theta_n = t - t_{n-1}$, the occurrence probability of θ_n (i.e., that there be no collision in time θ_n) being given by

$$W_n = e^{-\theta_n / t} \quad . \tag{I.10}$$

Putting all these results together one has for the contribution to $\langle \mu_z(t) \mu_z(0) \rangle$ due to all processes involving n collisions between time zero and t.

$$\langle \mu_z(t) \mu_z(0) \rangle_n^{(+)} = \frac{\tau \mu^2}{3} \int_0^\infty d\theta_1 \cdots \int_0^\infty d\theta_n \; \delta\left(t - \sum_{i=1}^{n} \theta_i\right)$$

$$\prod_{i=1}^{n} \left\{ \langle \cos \omega_i \theta_i \rangle \frac{e^{-\theta_i / \tau}}{\tau} \right\} \quad . \tag{I.11}$$

On the r.h.s. of this expression, the factor, 3, in the denominator arises from taking an average overall initial orientations (at t=0), and the delta function guarantees that the sum of all the intervals, θ_i, is equal to t. Finally, the superscript "(+)" on the l.h.s. depicts the

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fact that the relationship is valid only for positive time; otherwise the r.h.s. is manifestly zero.

With respect to negative times, it may be noted that, since the correlation function depends only on relative time, i.e.,

$$\langle \mu_z(t+t_0)\mu_z(t_0) \rangle = \langle \mu_z(t)\mu_z(0) \rangle \qquad (I.12)$$

one has

$$\langle \mu_z(-t)\mu_z(0) \rangle = \langle \mu_z(0)\mu_z(t) \rangle \quad . \qquad (I.12a)$$

Now, in a classical theory, $\mu_z(t)$ and $\mu_z(0)$ are c-numbers, so that the order in which they are written is immaterial. It then follows immediately that, for $t > 0$

$$\langle \mu_z(-t)\mu_z(0) \rangle = \langle \mu_z(t)\mu_z(0) \rangle$$

or

$$\langle \mu_z(t)\mu_z(0) \rangle = \langle \mu_z(|t|)\mu_z(0) \rangle^{(+)} \qquad (I.13)$$

the r.h.s. of (I.13) being given by (I.11).

With the aid of (I.13), one may rewrite the basic relationship (I.6) for α_i as

$$\alpha_i = \beta\omega \int_0^\infty \cos \omega t \, \langle \mu_z(t)\mu_z(0) \rangle \, dt \quad . \qquad (I.14)$$

Since, now, only positive times are involved, one may forthwith introduce

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(I.11) into (I.14); a subsequent time integration then yields (upon also summing over all interval numbers, n, from one to infinity).

$$\alpha_i = \frac{\beta\omega\tau\mu^2}{3} \mathcal{R} \sum_{n=1}^{} \prod_{i=1}^{n} \left\{ \int d\theta_i \left< \cos \omega_i \theta_i \right> \frac{1}{\tau} e^{-\theta_i(1/\tau + i\omega_i)} \right\}$$

$$= - \frac{\beta\mu^2}{3} \mathcal{I}_m \left\{ -i\omega\tau \sum_{n=1}^{\infty} \left< \frac{1-i\omega\tau}{(1-i\omega\tau)^2 + \omega_i^2\tau_i^2} \right>^n \right\} . \qquad (I.15)$$

The braces signifying the remaining average over each of the ω_i.

Concerning this average, it is undoubtedly most appropriate to assume (as in fact done in Gross's paper[6]) that the ω_i are each thermally distributed. However, in the interest of transparency, the simpler procedure of taking all the ω_i equal to one and the same angular speed, ω_r given eventually by an appropriate thermal average will be adopted.

Introducing, then, the replacement $\omega_i \to \omega_r$, and carrying out the sum over n, one obtains, after a little algebra

$$\alpha_i = - \frac{\beta\mu^2}{3} \mathcal{I}_m \left\{ \frac{(-i\omega\tau)(1-i\omega\tau)}{(-i\omega\tau)(1-i\omega\tau) + \omega_r^2} \right\} \qquad (I.16),$$

$$= - \frac{\beta\mu^2}{3} \mathcal{I}_m \left(1 - \frac{\omega_r^2}{\omega_r^2 - \omega^2 - i\omega/\tau} \right)$$

or, more explicitly,

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$$\alpha_1 = \frac{\beta\mu^2\omega_r^2}{3} \frac{\omega/\tau}{(\omega_r^2-\omega^2)^2 + \omega^2/\tau^2} \quad . \tag{I.17}$$

For the case in which

$$\frac{1}{\tau} << \omega_r, \omega \tag{I.18}$$

(which applies to our problem), and for ω not too close to ω_r (i.e., in the far wings of rotational lines), (1.17) reduces to

$$\alpha_1 = \frac{\beta\mu^2}{3} \frac{\omega_r^2 (1/\tau)}{\omega^3(1-\omega_r^2/\omega^2)^2} \approx \frac{\beta\mu^2}{3} \frac{\omega_r^2(1/\tau)}{\omega^3} \left(1 + \frac{2\omega_r^2}{\omega^2}\right). \tag{I.19}$$

At this point, it is desirable to take the thermal average over ω_r. For the case of a simple (linear) rotator, the weight function is

$$\omega_r \, e^{-\beta I\omega^2/2}$$

so that

$$\langle \omega_r^2 \rangle = \frac{2}{\beta I} \tag{I.20a}$$

$$\langle \omega_r^4 \rangle = 2\langle \omega_r^2 \rangle^2 \tag{I.20b}$$

and (I.19) becomes

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$$\alpha_i = \frac{2}{3} \; \frac{\mu^2}{I} \; \frac{1}{\tau\omega^3} \left[1 + \frac{4\langle\omega_r^2\rangle}{\omega^2} \right] \; . \tag{I.21}$$

A somewhat more useful form of (I.21) is achieved by expressing $\langle\omega_r^2\rangle$ in terms of the characteristic rotational constant,

$$B \equiv \frac{\hbar}{4\pi c I} \; . \tag{I.22}$$

From (I.22) and (I.20a), one has

$$\langle\omega_r^2\rangle = \frac{2}{\beta} \; \frac{4\pi c B}{\hbar} = \frac{8\pi k T c B}{\hbar}$$

and

$$\frac{\langle\omega_r^2\rangle}{\omega^2} = 4 \left(\frac{kT}{2\pi\hbar c} \right) \frac{B}{\bar{\nu}^2} \tag{I.23}$$

where ω has been expressed in wave numbers

$$\bar{\nu} = \omega/2\pi c \; .$$

Inserting (I.23) into (I.21), one has

$$\alpha_i = \frac{2}{3} \; \frac{\mu^2}{I} \; \frac{1}{\tau\omega^3} \left[1 + \frac{16B}{\bar{\nu}^2} \left(\frac{kT}{2\pi\hbar c} \right) \right] \; . \tag{I.24}$$

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It is now of interest to estimate the magnitude of the second term in the square bracket for the case of interest to us. Here the relevant numbers are $\bar{\nu} = 1000$ cm^{-1}, $kT/2\pi\hbar c \sim 300$ cm^{-1} and[43] $B \sim 30$ cm^{-1}. Inserting them into (I.24) gives for the second term ε magnitude ~ 0.15. Let us now note that the whole effect of rotational motion is contained in this term. The above numerology exhibits that this motion, although non-negligible is of secondary importance in determining the absorption at 10 microns. In particular it justifies the text procedure of replacing rotatory motion of the dipole by linear motion of a fictitious charged particle.

A final point concerns the values of charge and mass to be used for this fictitious particle. In the case of a diatomic rotator, one may express μ and I in terms of internuclear separation, R, as

$$\mu = eR$$

$$I = M_{red} R^2$$

(I.21) then becomes

$$\alpha_1 = \frac{2}{3} \frac{e^2}{M_{red}} \frac{1}{\tau\omega^3} \left[1 + \ldots \right] \; . \qquad (I.25)$$

The corresponding expression for the real part σ_R of the complex "conductance", $\sigma = -i\omega\alpha$ (i.e., $\sigma_R = \omega_{\leftarrow 1}$) reads

$$\sigma(\omega) = \frac{2}{3} \frac{e^2}{M_{red}} \frac{1}{\tau\omega^2} \left[1 + \ldots \right] \qquad (I.26)$$

which, apart from the correction term in the square bracket (discussed above) and the factor 2/3 (reflecting the fact that the number of degrees

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of rotational motion is two, as compared with three for translation) is just the well-known Drude formula for absorption associated with the (impact) collision-interrupted motion of a free particle of charge e and mass M_{red}. It is thus clear that whenever the ratio e^2/M_{red} occurs in text equations[44], the appropriate replacement recipe is:

$$\frac{e^2}{M_{red}} \longrightarrow \frac{\mu^2}{I} \quad . \tag{I.27}$$

APPENDIX II

In this appendix, the integral in the text Eq. (2.56) will be evaluated by the method of steepest descents. The integral in question is of the form

$$\mathcal{Q} = \int_0^\infty e^{-bF(y)} \, dy \qquad (II.1)$$

where

$$F(y) = ay + 1/\left[y^{1/2} + (y+1)^{1/2} \right] \qquad (II.2)$$

(the dimensionless parameters, a and b, being defined by the text Eqs. (2.57b) and (2.57c), respectively).

The first step is to locate the saddle-points, as defined by the equation

$$F'(y) = 0 \, . \qquad (II.3)$$

Differentiating (II.2), one has

$$F'(y) = a - \frac{y^{-1/2} + (y+1)^{-1/2}}{2\left[y^{1/2} + (y+1)^{1/2} \right]^2}$$

which, after a few algebraic manipulations, takes the form

$$F'(y) = a - \frac{1}{2y^{1/2}(y+1)^{1/2}\left[y^{1/2} + (y+1)^{1/2} \right]} \, . \qquad (II.4)$$

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Introducing (II.4) into (II.3), one obtains the saddle-point equation

$$a = \frac{1}{2y_s^{1/2} (y_s+1)^{1/2} \left[y_s^{1/2} + (y_s+1)^{1/2} \right]}$$ (II.5)

(the subscript, s, denoting the saddle point values[45] of y).

The usual procedure is to solve for y_s in terms of the (physically variable) parameter, a. In view of the complicated algebraic form of (II.5), the (equally appropriate) procedure of regarding y_s to be the basic parameter — given in terms of physical quantities via (II.5) and the text Eq. (2.57b) will be followed.[46]

The next step is to develop a Taylor expansion of F(y) about y_s (up to and including terms quadratic in $y-y_s$). For this, $F''(y_s)$ is required. Differentiating (II.4), and using (II.5) (together with algebraic manipulations of the type employed in establishing the final form of (II.5)), one obtains

$$F''(y_s) = \frac{a}{2} \left[\frac{1}{y_s} + \frac{1}{y_s+1} + \frac{1}{y_s^{1/2}(y_s+1)^{1/2}} \right]$$ (II.6)

Using the standard steepest-descents approximation of replacing F(y) by its Taylor-expansion in the vicinity of the saddle point, and extending the lower limit of integration to minus infinity, one has

$$\mathcal{L} \doteq \int_{-\infty}^{+\infty} e^{-b \left[F(y_s) + \frac{1}{2} F''(y_s)(y-y_s)^2 \right]} dy$$

$$= \left[\frac{2\pi}{bF''(y_s)} \right]^{1/2} e^{-bF(y_s)}$$ (II.7)

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where $F''(y_s)$ is given by (II.6), and where

$$F(y_s) = a \, y_s + \frac{1}{y_s^{1/2} + (y_s+1)^{1/2}}$$

$$= a \left[y_s + 2y_s^{1/2} \, (y_s+1)^{1/2} \right] \tag{II.8}$$

(the second equality arising from use of (II.4)).

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1. R. M. Goody, Atmospheric Radiation I. Theoretical Basis (Oxford 1964) Section 5.4.7 (pp. 195-196).

2. High Intensity Laser Propagation in the Atmosphere, TRW Systems Group (Final Report 05691-6003-R000) Chapter I.

3. Summary of May 16, 1967 meeting on Infrared Atmospheric Absorption, p. 2.

4. It should be stated that the inadequacy in question refers specifically to H_2O - H_2O collision-broadening; the theory may still find application to a variety of other cases (e.g., broadening by collisions of H_2O with nonpolar gases).

5. I.E., subject only to the requirement that the angular velocity vectors before and after collision by perpendicular to the momentary dipole orientation vector.

6. E. P. Gross, J. Chem. Phys. 23, 1415 (1956).

7. In particular this method is more closely related to the detailed calculations of this paper than the Boltzmann equation approach.

8. As shown in detail in the appendix paragraph subsequent to Eq. (I.24), this is the case for our problem.

9. Mathematically, the intensity is proportional to the absolute square of the Fourier transform of the electric current. As is known, the magnitude of said transform is determined principally by time variations on a scale of $1/\omega$ (or less).

REFERENCES (continued)

10. The last assumption is appropriate for our case, if the collisions of interest are between the absorbing molecule (H_2O) and the principal atmospheric constituents (N_2 or O_2). For H_2O-H_2O collisions, the assumption is still qualitatively appropriate.

11. In the case of H_2O, the most relevant interactions — i.e., those affecting the rotational motion are those between each H atom and the perturbing molecule. Ignoring H_2O-H_2O collisions, — i.e., focusing on the collisions involving the principal atmospheric constituents — O_2 and N_2, one may assume the interactions to be mainly of two types; (a) an attractive polarization type interaction ($\sim 1/r^4$), arising from the partially ionic character of H_2O (with each hydrogen atom having a net charge $e \sim e$) and (b) a repulsive interaction which will be assumed to have the exponential form given by Eq. (1.4). Provisionally the polarization term will also be neglected; the general question of attractive forces will be considered later — especially in connection with H_2O-H_2O collisions.

12. Eq. (1.107) of Ref. 2.

13. It is expected that a recipe similar to that used in Ref. 2 will be found adequate for our purposes.

14. Here, and in what follows, only $\phi^{(+)}$ will be treated explicitly; the results for $\phi^{(-)}$ will be found to be almost automatically inferable from those for $\phi^{(+)}$.

15. It may be remarked in passing that this last feature corresponds completely to the well known classical proportionality between the amplitudes for either absorption or stimulated emission processes and the acceleration of the charged particles involved. In the case at hand, this acceleration is (in zero[th] order) $- \frac{1}{M} \frac{\partial V(x)}{\partial x}$.

REFERENCES (continued)

16. The ratio k_f/k_i arises from the circumstance that the outgoing and incident waves are characterized by different velocities, their ratio being k_f/k_i. The factor 4 occurs simply by virtue of the asymptotic form of $\psi_i(x)$, as given by (2.10), the incident amplitude of which is

    $$\frac{1}{2} e^{-i(k_i x + \delta_i)} .$$

16a. It is here tacitly assumed that the potential, $V(x)$, is sufficiently repulsive so that ψ_i, ψ_f, and ψ_{sc} all drop exponentially with diminishing x, once inside their respective classical turning points. This property in question certainly holds for a potential of the form $V(x) \propto e^{-\alpha x}$.

17. A standard reference is Morse and Feshback, "Methods of Theoretical Physics" (McGraw-Hill, 1953), Vol. II, page 1687, et seq. The case at hand, namely the one-dimensional repulsive potential, is treated explicitly in Ref. 2 [pp 14-15 and Eq. (I.35)].

18. Tables of Integral Transforms, Bateman Manuscript Project (McGraw-Hill, 1954), Vol. I.

19. ΔE_ω will ultimately be interpreted as the absorbed energy per "effective" collision. Its product with the "effective" collision rate, $1/\tau_{eff}$, will represent the rate, W, of energy absorption from the field per absorbing molecule; dividing W by the magnitude of the Poynting flux vector of the electromagnetic field will then yield the ultimate goal of the calculation, namely the absorption cross-section of the polar molecule.

20. Since our calculation may be regarded as a lowest-order Born approximation (with the electromagnetic field providing the perturbation which causes transitions between exact eigen-states of the field-free system, microscopic reversibility (symmetry with respect to interchange of initial and final state indices, k_i and k_f is an immediate consequence. (Note, incidentally, that (2.40) is manifestly symmetric with respect to such interchange.)

21. $I(k_i)dk_i$ is seen in (2.43) to be equal (apart from the normalization factor) to the spectral component of the particle flux at k_i. In this connection, it will be recalled that $P_{(+)}$ $(k_i \rightarrow k_f)$ is defined in terms of the ratio of incoming to outgoing particle flux.

22. Cf. Ryshik and Gradstein, Tables (Deutsche Verlag der Wissenshaften, 1963), formulae 7.322 and 7.335.

23. In Drude's theory, absorption (in the wing-region, $\omega\tau \gg 1$) is proportional to the real part of the conductivity. This quantity is given by the formula

$$\sigma(\omega) = \frac{e^2}{M\omega^2} \frac{1}{\tau}$$

(per charge carrier). Corresponding to this real part, there exists a nonvanishing energy transfer from the electromagnetic field to the charged particle, given by

$$2\sigma(\omega)\mathcal{E}_o^2 = \frac{2e^2}{M\omega^2} \frac{1}{\tau} \; \mathcal{E}_o^2 \; .$$

Dividing by the incident flux, $c\mathcal{E}_o^2/2\pi$ one then has for the absorption cross section,

$$Q = \frac{e^2}{\pi M c \omega^2 \tau} \quad , \text{ q.e.d.}$$

With regard to the factor 4/3, occurring in (2.52) it should be pointed out that the factor $1/\tau$ in Drude's expression actually denotes the momentum-transfer collision rate, and should thus be equated to the total collision rate times the factor $\langle 1 - \cos \psi \rangle$ (where ψ is the scattering angle). Now it is a relatively straight-forward exercise to show that, in specular reflection from a plane surface, an average over all possible angles of incidence, $\langle \cos \psi \rangle = -1/3$; hence $\langle 1 - \cos \psi \rangle = 4/3$.

24. The circumstance that (2.55) is an impact-type expression should not be surprising, since the physical significance of its condition for validity (namely $\frac{2\pi\omega}{\alpha(v_i+v_f)} \ll 1$) is simply that an appropriately defined "collision time" (in this case, the interaction range, $1/\alpha$, divided by some average velocity, $(v_i+v_f)/2$) be small compared to the reciprocal of the external frequency, ω. This condition is one of the standard criteria for the applicability of impact-type theories (cf. T. Holstein, Phys. Rev. 79, 744 (1950).

25. For this table kT and M were set equal to 300°K and twice the hydrogen-atom mass, respectively.

26. As remarked in the introduction, even this upper limit will be found to be substantially smaller than the experimental value for H_2O far-wing absorption reported by Burch.[3]

27. This formula actually gives the r.m.s. relative velocity, but is sufficiently accurate for our purposes.

28. Actually, the quoted paragraph gives this condition as $(\omega-\omega_o) \tau_c < 1$, where ω_o is the unperturbed line frequency. In our problem, as discussed lengthily in Appendix I, this frequency (i.e., any one of the dominant rotational frequencies) is set equal to zero.

29. In the case at hand, one has to consider the perturbation of the rotational frequencies (or, more generally, the rotational motion, itself) arising during the transient existence of the H_2O-H_2O collision-complex.

30. In the actual physical problem, this would correspond to the distance of closest approach of the one of the hydrogen atoms to the nearest atom of the perturbing molecule (e.g., in H_2O-H_2O collisions the closest distance of approach of one hydrogen atom of the first H_2O

REFERENCES (continued)

    molecule to the oxygen atom of its collision-partner). Said distance, as well as the magnitude of V_a, may ultimately be estimated by various methods (e.g., structure and hydrogen-bond energies in ice and liquid water).

31. This statement implies, of course, that one doesn't take $V_a(x)$ to be literally constant; otherwise it would cancel out of the problem. One has always to understand the assumed constancy in the limiting sense in which $V_a(\infty)$ is still zero.

32. The characteristic ω^{-2} dependence of (3.16) of classical impact theory manifestly obtains in the limit $\hbar\omega \to 0$.

33. Strictly speaking, we should set $V(r_o)$ equal to the initial relative kinetic energy of the two molecules. However, as will be seen aposteriori; the individual magnitudes of the attractive and repulsive components of (3.20) are sufficiently large so that said relative kinetic energy represents but a small correction.

34. Only the barest outlines can be given at this time, since no specific calculations have as yet been carried out. It is hoped to have something more definite for the final report.

35. In particular, there are actually _two_ potential minima, each of which are characterized by the formation of the well-known hydrogen-level configuration: $0 \text{—} H \text{---} 0$.

36. cf. G. C. Pimental and A. L. McClellan, _The Hydrogen Bond_, (Freeman and Co., 1960), p. 126.

37. The justification for the use of this theory, as well as all other developments of the hindered-rotation approach, will have to be reserved for the final report.

REFERENCES (continued)

38. It is herewith once and for all assumed that the (field-free) Hamiltonian of the system is such that there is no preferred spatial direction. Thus, any cartesian component may be used; in fact $|<n|\mu_z m>|^2$ will eventually be replaced by $\frac{1}{3} |<n|\mu|m>|^2$.

39. Literally, s arises from the recipe that the field be slowly "turned on" (as e^{st}); as is known, such a recipe leads to a correct description of dissipative effects. In the standard Kramers-Heisenberg formula, the fact that the energy denominators $E_n - E_m \pm \hbar\omega$ are nonzero permits one to go to the limit $s = 0$.

40. (I.5a) is of course violated for the problem of interest to us, but should be adequate for the restricted goal of this appendix, namely, a study of the adequacy of replacing rotational motion by linear motion.

41. As has been pointed out sometime ago by E. P. Gross, J. Phys. Chem. **23** p. 1415 (1955), this latest feature of "conservation of orientation" is contradicted by the "strong-collision" model of van Vleck and Weisskopf, Rev. Mod. Phys. 1948, 1946, which assumes complete disorientation per collision. Incidentally, although the present treatment differs from the Boltzmann equation approach of Gross, it leads to equivalent results.

42. In a stochastic theory, the symbol $\langle....\rangle$ acquires the meaning of a mixed stochastic-thermodynamic average, the stochastic aspect consisting of averaging over all stochastic possibilities with appropriate weights.

43. Actually, in the case of water vapor, when rotational motion is that of an asymmetric top, three rotational constants (corresponding to the three moments of inertia) exist. The value given here is that which appears to be the most relevant for rotation of the dipole-moment.

44. In these equations, the subscript "red" is dropped for notational convenience.

45. Inspection shows that the r.h.s. of (II.5) is monotonic; there is hence only one value for the saddle point, y_s.

46. The value y_s for a particular value of the parameter, a, may ultimately be determined by any convenient numerical or graphical procedure.

Chapter 2.

STIMULATED RAMAN EFFECT

1. INTRODUCTION

In a previous report[1] the general time dependence of Raman back-scattered waves was considered and applied to the specific problem of the self-quenching of a very intense laser beam in the atmosphere. In this report we shall first review some of the general results obtained previously. Next, we shall describe the action of a Raman amplifier. Finally, an attempt to quantitatively describe a recent experiment[2] in Raman pulse generation will be presented. The research for this last description has not, as yet, been completed.

Let us consider the interaction of a beam of laser light passing through a length of Raman active substance, with a beam of light at the first Stokes frequency of the laser light in that substance. If the second beam is traveling in a direction which is opposite to the first it will be amplified by the stimulated emission of backscattered light. Assuming that all dissipative processes — including the stimulated emission of forward scattered Raman photons— are inconsequential (i.e., they contribute a negligible amount to the depletion of the laser beam intensity within the length of Raman active material considered) then the densities of the laser photons $\rho_\ell(x,t)$ and amplified backscattered Raman photons $\rho_b(x,t)$ in the substance are related by the rate equations[1]

$$\left(\frac{\partial}{\partial t} + c\,\frac{\partial}{\partial x}\right)\rho_\ell = -\rho_\ell(\alpha\rho_b + \beta) \tag{1}$$

$$\left(\frac{\partial}{\partial t} - c\,\frac{\partial}{\partial x}\right)\rho_b = +\rho_\ell(\alpha\rho_b + \beta) \tag{2}$$

where

$$\alpha = \frac{c^3}{2\nu^2 \Delta\nu}\, c\rho_T \sigma(\pi) \quad \text{and} \quad \beta = c\rho_T \sigma(\pi)\,\frac{\Omega_o}{4\pi} \ .$$

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The quantity $\sigma(\pi)$ is the Raman backscattering cross section, ρ_T is the number density of the medium, $\Delta\nu$ is the line width of the amplified wave and Ω_o is the effective solid angle for Raman amplification — Ω_o will be discussed in greater detail later in this report. The change of variables

$$s = t - \frac{x}{c} \ , \quad \tau = t + \frac{x}{c} \ ,$$

$$R_\ell(s,\tau) = \rho_\ell(x,t) \ , \quad R_b(s,\tau) = \rho_b(x,t) \ ,$$

enables us to write Eqs. (1) and (2) as

$$2\frac{\partial R_\ell}{\partial \tau} \ = \ -R_\ell(\alpha R_b + \beta) \tag{3}$$

$$2\frac{\partial R_b}{\partial s} \ = \ R_\ell(\alpha R_b + \beta) \tag{4}$$

The general solution of these equations is given by

$$R_\ell(s,\tau) \ = \ \frac{\dot{F}(s)}{G(\tau) - \frac{\alpha}{2} F(s)} \ , \tag{5}$$

$$R_b(s,\tau) \ = \ -\frac{\beta}{\alpha} + \frac{2}{\alpha} \frac{\dot{G}(\tau)}{G(\tau) - \frac{\alpha}{2} F(s)} \tag{6}$$

where F and G are arbitrary functions and $\dot{F}$ and $\dot{G}$ are the derivatives of these functions with respect to their arguments.

Equations (5) and (6) have been obtained previously. The application of boundary conditions to these equations in such a way as to describe first a Raman amplifier, and then a Raman pulse generator, is the subject of this report.

2. THE RAMAN AMPLIFIER

Consider a situation in which a Raman active material occupies the slab $0 \leq x \leq L$. Let laser light of constant intensity be incident on this slab from the left so that

$$\rho_\ell(0,t) = \rho_o \tag{7}$$

for all time. At $t = 0$ the slab is irradiated on the right by a beam of light at the first Stokes frequency of the laser light in the substance. The photon density of the Stokes light is given by $R(t)$:

$$R(t) = \rho_b(L,t) , \quad R(t) = 0 \text{ for } t < 0. \tag{8}$$

For the purposes of this section we shall assume that the spontaneous creation of backscattered photons in the amplifier is negligible, so that we may neglect β in Eq. (6). Defining the quantity

$$\eta(t) = \frac{\alpha}{2} \int_{-\infty}^{t} dt' \, R(t') \tag{9}$$

we may employ Eqs. (5) and (6) to rewrite the boundary conditions (7) and (8) in the form:

$$\frac{\dot{F}(t)}{G(t) - \frac{\alpha}{2} F(t)} = \rho_o , \tag{10}$$

$$\frac{\dot{G}(t + \frac{L}{c})}{G(t + \frac{L}{c}) - \frac{\alpha}{2} F(t - \frac{L}{c})} = \dot{\eta}(t) . \tag{11}$$

Equation (11) may be written as

$$\dot{G}(t + \frac{L}{c}) - \dot{\eta}(t) \, G(t + \frac{L}{c}) = -\frac{\alpha}{2} \dot{\eta}(t) \, F(t - \frac{L}{c}) . \tag{12}$$

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Defining the quantity

$$g = \frac{\alpha}{2} \rho_o , \tag{13}$$

solving Eq. (10) for $G(t)$, and substituting the results in Eq. (12) we obtain the differential difference equation for $F(t)$:

$$\ddot{F}(t + \frac{L}{c}) + [g - \dot{\eta}(t)] \dot{F}(t + \frac{L}{c}) - g\dot{\eta}(t)F(t + \frac{L}{c})$$

$$= - g\dot{\eta}(t)F(t - \frac{L}{c}) \tag{14}$$

This equation may be concisely solved in terms of the quantity

$$E(t) = \dot{F}(t) e^{gt} . \tag{15}$$

Equations (5) and (6) imply that we may arbitrarily choose $E(0)$ equal to unity. Equation (14) may be rewritten in the form

$$E(t) = 1 + \theta(t - \frac{L}{c}) e^{2g\frac{L}{c}} \int_0^{t-\frac{L}{c}} dt'' \dot{\eta}(t'') e^{gt''} + \eta(t'')$$

$$\cdot \left\{ 1-g \int_0^{t''} dt' E(t'- \frac{L}{c}) e^{-gt'} -\eta(t') \right\} , \tag{16}$$

where $\theta(t) = 1$ for $t > 0$ and $\theta(t) = 0$ for $t < 0$. Equation (16) relates the value of the function $E(t)$ at a time t to its values at times less than $t - 2\frac{L}{c}$. Since

$$E(t) = 1 \quad \text{for } t \leq \frac{L}{c} \tag{17}$$

we may step-wise extend our knowledge of $E(t)$ in time intervals of duration $2\frac{L}{c}$ by first inserting Eq. (17) into Eq. (16) to give

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$$E(t) = 1 + \theta(t - \frac{L}{c})\, e^{2g\frac{L}{c}}$$

$$\left\{ \eta(t - \frac{L}{c}) + \int_0^{t - \frac{L}{c}} dt''\, \eta(t'') \int_0^{t''} dt'\, \eta(t')\, e^{g(t''-t') + \eta(t'') - \eta(t')} \right\}$$

$$\text{for } t \le 3\,\frac{L}{c}, \qquad (18)$$

and then inserting Eq. (18) into Eq. (16) to give $E(t)$ for $t \le 5\,\frac{L}{c}$, etc.

The laser and Raman photon densities at any point in the amplifier are related to $E(t)$ in the following manner

$$R_\ell(s, \tau) = \rho_0 \frac{\dot{E}(s)}{E(s) + \int_s^\tau dt'\, e^{g(s-t')}\, \dot{E}(t')}, \qquad (19)$$

$$R_b(s, \tau) = \frac{2}{\alpha}\left(e^{-2g\frac{x}{c}} \right) \frac{E(\tau)}{E(s) + \int_s^\tau dt'\, e^{g(s-t')}\, \dot{E}(t')}. \qquad (20)$$

The amplified signal is given by

$$\rho_b(o, t) = \frac{2}{\alpha} \frac{\dot{E}(t)}{E(t)}. \qquad (21)$$

Equations (16) through (21) describe the behavior of the amplifier for an arbitrary pulse. As an illustrative example let us consider an input square pulse of infinite duration and photon density ρ_1; i.e., let

$$\rho_b(L, t) = \frac{2}{\alpha} \dot{\eta}(t) = \frac{2}{\alpha} h\theta(t) = \rho_1\theta(t), \qquad (22)$$

where $h = \alpha\rho_1/2$ by definition.

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In this case Eq. (18) gives

$$E(t) = 1 + \frac{h \, e^{2g\frac{L}{c}}}{(g+h)^2} \left\{ h \left[e^{(g+h)(t-\frac{L}{c})} - 1 \right] + (g+h)g(t-\frac{L}{c}) \right\} \tag{23}$$

for $L/c \leq t \leq 3\,L/c$, and Eq. (21) yields

$$\rho_b(0,t) = \rho_1 \frac{(g+h)\left[h \, e^{(g+h)(t-\frac{L}{c})} + g \right]}{h\left\{ h\left[e^{(g+h)(t-\frac{L}{c})} - 1 \right] + (g+h)(t-\frac{L}{c}) \right\} + (g+h)^2 \, e^{-2g\frac{L}{c}}} \tag{24}$$

in that same interval. Equation (24) exhibits the gain and "pulse-width sharpening" characteristic of laser amplifiers. Expanding the amplified signal about its time of arrival (L/c) we find that

$$\rho_b(0,t+\frac{L}{c}) \xrightarrow[t \to 0]{} \rho_1 \, G\{1 - (G-1)ht + \dots\} \, , \tag{25}$$

where

$$G = e^{2g\frac{L}{c}} = e^{\alpha\frac{L}{c}\rho_o} \tag{26}$$

is the amplifier gain.

The step-wise integration of Eq. (14) indicated by Eq. (16) is useful for pulses which are no longer than several times $2\,L/c$ (note, for $L = 30$ cm., $2\,L/c = 2$ nanoseconds). For very long pulses the large number of integrations required to describe the amplified pulse at late times would, of necessity, produce considerable difficulties. However, for the input square pulse of infinite duration described by Eq. (22) some simplifications can be made and an analytic expression for $E(t)$ for all times may be obtained. Substituting Eqs. (15) and (22) into Eq. (14) we obtain

$$\ddot{E}(t+\frac{L}{c}) - (g+h)\dot{E}(t+\frac{L}{c}) = -gh \, e^{2g\frac{L}{c}} E(t-\frac{L}{c}) \tag{27}$$

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with

$$E(t) = 1 \text{ for } t \leq \frac{L}{c} \text{ and } \dot{E}(\frac{L}{c}) = h \, e^{2g\frac{L}{c}} \tag{28}$$

Defining the Laplace transform of $E(t+\frac{L}{c})$ by

$$\hat{E}(p) = \int_0^\infty dt \, e^{-pt} \, E(t+\frac{L}{c}) \tag{29}$$

we readily obtain

$$\hat{E}(p) = \frac{1}{p} + h \, e^{2g\frac{L}{c}} \, \frac{p-g}{p \, D(p)} \tag{30}$$

where

$$D(p) = p^2 - (g+h) \, p + gh \, e^{2\frac{L}{c}(g-p)} . \tag{31}$$

We may use the Bromwich integral

$$E(t+\frac{L}{c}) = \frac{1}{2\pi i} \int_{d-i\infty}^{d+i\infty} dp \, e^{pt} \, \hat{E}(p) , \tag{32}$$

where d is such that the contour lies to the right of all the poles of $\hat{E}(p)$, to express $E(t + \frac{L}{c})$ in terms of the finite sum

$$E(t+\frac{L}{c}) = 1 + h \, e^{2g\frac{L}{c}} \sum_{n=0}^{N} (-gh)^n \, e^{2\frac{L}{c}n} \, A_n(t-2\frac{L}{c}n) , \tag{33}$$

$$\text{for } N \leq \frac{ct}{2L} \leq N+1, \ N = \text{integer}, \tag{33}$$

where

$$A_n(t) = -\frac{1}{(n+1)!} \frac{d^{n+1}}{dp^{n+1}} \left[\frac{(p-g)}{(p-g-h)^{n+1}} \, e^{pt} \right] \Bigg|_{p=o}$$

$$+ \frac{1}{n!} \frac{d^n}{dp^n} \left[\frac{p-g}{p^{n+2}} \, e^{pt} \right] \Bigg|_{p=g+h} . \tag{34}$$

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This result is completely equivalent to that obtained from Eq. (16). It is much simpler to obtain and express analytically, but still quite difficult to employ for $N \gg 1$. In that case $E(t)$ can be obtained from Eq. (32) by appropriately distorting the integration path. For $2 L/c \neq t_o = h^{-1} - g^{-1}$ the result is

$$E(t + \frac{L}{c}) \xrightarrow[t \to \infty]{} h \, e^{2g\frac{L}{c}} \, \frac{p_o - g}{p_o D'(p_o)} \, e^{p_o t} \, , \tag{35}$$

where p_o is the pole of $(p-g)/D(p)$ with the largest real part. It can be shown that p_o is on the real axis and is a zero of $D(p)$ (but not the zero $p=g$). The pole p_o is obtained graphically (see Figs. IIa and IIb) by plotting the parabola $(g + h)p - p^2$ and the exponential $gh \exp[2L(g-p)/c]$ versus p for p real. These curves intersect twice: once at $p=g$ and once at $p=p_o$. Examining these curves we find that for $2L/c < t_o$, $0 \leq p_o < g$, and for $2L/c > t_o$, $g < p_o < g + h$. Using Eq. (35) in Eqs. (19) and (20) we obtain

$$\rho_\ell(x,t) \xrightarrow[t \to \infty]{} p_o \, \frac{g-p_o}{g-p_o \, e^{-2(g-p_o)x/c}} \, , \tag{36}$$

$$\rho_b(x,t) \xrightarrow[t \to \infty]{} \frac{2}{\alpha} p_o \, \frac{p_o - g}{p_o - g \, e^{2(g-p_o)x/c}} \, . \tag{37}$$

from which — with the aid of $D(p_o) = 0$ — it is easy to show that

$$\rho_\ell(L,t) \xrightarrow[t \to \infty]{} p_o + \rho_1 - \frac{2}{\alpha} p_o \, , \tag{38}$$

$$\rho_b(0,t) \xrightarrow[t \to \infty]{} \frac{2}{\alpha} p_o \, . \tag{39}$$

Equations (36) and (37) — describing ρ_ℓ and ρ_b in the interior of the amplifier after a very long time — are graphically displayed in Fig. III.

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Equation (39) indicates that although the leading edge of the input pulse described by Eq. (22) may be amplified to a value greatly in excess of $\rho_o + \rho_1$ the tail of the pulse is always given by $2p_o/\alpha \leq \rho_o + \rho_1$. The sum of Eqs. (38) and (39) leads to the statement of conservation of energy: $\rho_\ell(L,t) + \rho_b(0,t) = \rho_o + \rho_1$.

3.   THE RAMAN PULSE GENERATOR

In this section we shall employ a model, based on Eqs. (5) and (6), and the theory of "self-trapping,"[3,4] to quantitatively describe the results of an experiment performed by Maier, et al.[2] In this experiment a carbon disulfide cell was illuminated by a beam of laser light. Observations at the entrance of the cell revealed intense short pulses of backward scattered Stokes radiation. These pulses had a duration $\sim 3 \times 10^{-11}$ sec and a peak power one order of magnitude higher than the incident laser power. Since the gain in the CS_2 cell was quite large, it is not surprising that the emitted pulse was very intense. However, the mechanism for the production of the initiating pulse of backscattered Stokes radiation remains to be explained. The obvious candidate for such a mechanism is spontaneous emission. However, it has been previously demonstrated[1] that if a backscattered Raman wave in a uniform laser beam was generated solely by the spontaneous emission in that beam, then the intensity of the Raman beam cannot exceed that of the input laser beam (a physical explanation of this phenomena will be given later). Maier, et al., suggest that "A probable mechanism for the initiation of the pulse is the abrupt onset of backward stimulated Stokes emission near the exit cell surface, accompanying the occurrence of laser self-focusing in that region." In support of this suggestion they report that in measurements of the dependence on cell length of the laser threshold power for pulse formation, they found a result which was characteristic of the self-focusing effect. As further support for this suggestion we shall construct a specific model of the influence of self-focusing on the amplification of spontaneously emitted Raman waves. The validity of our model may be measured by the degree of success we attain in predicting the height and shape of the emitted pulse.

Consider first a Raman active medium and a beam of laser light incident on it from the left. Let the photon density of the incident beam

be the constant ρ_o and let the time of incidence be $t = 0$. The boundary
conditions are

$$\rho_\ell(0,t) = \rho_o \theta(t), \quad \rho_b(x,t) = 0 \text{ for } t \leq 0. \tag{40}$$

Equation (4) indicates that R_b is a continuous function of s and hence,
since $\rho_b = 0$ for $t < 0$ we have

$$R_b(0,\tau) = 0 . \tag{41}$$

Using Eqs. (40) and (41) in (5) and (6) we have[1]

$$\rho_b(x,t) = \rho_o \theta(s) \beta \frac{1 - e^{-(g+\beta/2)s}}{(g+\beta/2) e^{\beta x/c} -g+g \, e^{-(g+\beta/2)s}} . \tag{42}$$

Defining t_o to be the time required for the medium to generate a Raman
wave at the entry plane which is half the intensity of the incident wave,
i.e.,

$$\rho_b(0,t_o) = \frac{1}{2} \rho_o , \tag{43}$$

we obtain the relation

$$t_o(\rho_o) = \frac{2}{\alpha \rho_o} \ln(\frac{\alpha \rho_o}{\beta}) \tag{44}$$

to an excellent approximation. From Eq. (44) it is clear that t_o de-
creases with increasing ρ_o; ie., as the intensity of the incident wave
is increased, the time required to generate a Raman wave equal to half
the intensity of the incident wave is decreased.

Consider now an arrangement in which a laser beam is incident from
the left on a Raman active medium which occupies the space $x > 0$, and
propagates through the medium for a distance L maintaining a constant
cross sectional area (see Fig. IV). At $x = L$ the beam cross section is

assumed to decrease radically due to self trapping. Let the laser and Raman photon densities be denoted by $\rho_{\ell 1}$ and ρ_1 for $0 < x < L$, and $\rho_{\ell 2}$ and ρ_2 for $x > L$. For conservation of flux

$$\rho_{\ell 2}(L,t) = \lambda \, \rho_{\ell 1}(L,t) \tag{45}$$

by hypothesis. In Eq. (45), $\lambda \gg 1$ is the ratio of the beam area in region 1 to that in region 2. Self focusing occurs because the laser beam is sufficiently intense to induce significant changes in the index of refraction. These changes are large enough to induce a lens-like condition in the region about $x = L$. The initial laser beam in region 1 is consequently focused into a beam of a much smaller diameter in region 2. In region 2 the focusing effect of the increased index of refraction is exactly compensated for by the defocusing effect of diffraction and the beam propagates with a constant cross sectional area. Assuming that dispersion is sufficiently small, we may apply the principle of optical reversibility to those Raman photons which are spontaneously emitted within the cone angle for amplification in region 2. That is, upon incidence from the right on the region about $x = L$ they will be defocused by the same factor as that for focusing the laser beam incident upon this region from the left. These considerations lead to the boundary condition

$$\rho_2(L,t) = \lambda \, \rho_1(L,t) \, . \tag{46}$$

In a beam of uniform cross section the spontaneous emission is produced at a uniform rate along the beam. Consider two photons spontaneously emitted at x_1 and x_2 with $x_1 < x_2$. As they travel to the left they will be amplified. When the intensity of the wave emitted at x_2 is comparable to the initial laser intensity the wave emitted at x_1 also has an intensity comparable to the initial laser intensity. The laser intensity at location of the x_2-wave is therefore depleted and the gain is decreased. Consequently, a saturation effect occurs and the x_2-wave is prohibited from exceeding the initial laser wave in intensity. Since

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x_1 and x_2 were chosen arbitrarily the above argument holds throughout the beam and the backscattered spontaneous Raman beam cannot exceed the initial laser beam in intensity. This consequence of Eqs. (1) and (2) was previously demonstrated in a purely mathematical fashion.[1] In a beam of nonuniform cross section which, for example, corresponds to the self-trapping arrangement discussed above, the backscattered wave in the region $x > L$ will grow to the laser intensity in that region before a large decrease of the laser intensity in the region $0 < x < L$ can occur. This fact is a clear consequence of Eq. (44) and the fact that the laser intensity is much greater in region 2 than region 1. The backscattered wave will propagate through the plane at $x = L$ and will reappear to the left of this plane with an intensity comparable to the laser intensity there. Since the gain in region 1 is as yet undiminished the backscattered wave will now be amplified to an intensity far in excess of the initial laser intensity.

The physical argument given above is readily translated into a quantitative description of the Raman pulse. Eqs. (3) and (4) are valid in regions 1 and 2 separately if they are modified to include the fact that the constant "β" is different in the two regions. Consequently, $R_{\ell 1}$ and R_1 may be expressed in terms of F_1, G_1 and β_1 through Eqs. (5) and (6). This is also true for $R_{\ell 2}$, R_2, F_2, G_2 and β_2. The constants "β" differ by the factor Ω - the effective solid angle for Raman amplification. The effective solid angle "Ω_1" is obtained in the usual manner[1] for a beam of length L and a given cross section. The effective solid angle "Ω_2" corresponds to that of a cone with a half angle equal to the angle of total internal reflection in region 2. Since there are four independent functions ($F_{1,2}$ and $G_{1,2}$) four boundary conditions are required. Two boundary conditions are given by Eqs. (45) and (46). A third condition describes the source function. For simplicity we may take

$$\rho_{\ell 1}(0,t) = \rho_o \, \theta(t) . \tag{47}$$

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The final condition is that there is no radiation at the frequency of the Raman waves incident on the system from the right; i.e.,

$$R_2(0,\tau) = 0 .\tag{48}$$

Using Eqs. (45) through (48) in the modified Eqs. (5) and (6) leads to an expression for $\rho_1(0,t)$ in terms of a function which is the solution of a differential difference equation as in the preceding section. Since the theory of self-focusing[4] gives us a relationship between ρ_o and L, it is possible to determine the height and shape of the exciting pulse solely in terms of the incident laser intensity and λ.

The program outlined above for describing the backscattered pulse has not as yet been carried out because of some difficulties in solving the differential difference equation. As an aid in gaining insight into the nature of the solution to the above boundary value problem a simpler problem has been solved. This simpler problem is a mixed boundary-initial value problem. For this latter problem all space (i.e., $-\infty < x < \infty$) is filled with Raman active material. The self focusing occurs at $x = 0$ (in contrast to $x = L$ in the preceding problem) so that

$$\rho_{\ell 2}(0,t) = \lambda \rho_{\ell 1}(0,t) , \rho_2(0,t) = \lambda \rho_1(0,t) .\tag{49}$$

Initially the Raman and laser waves are arranged so that

$$\rho_{\ell 1}(x,0) = \rho_o , \rho_{\ell 2}(x,0) = \rho_1(x,0) = \rho_2(x,0) = 0 .\tag{50}$$

Equation (48) is valid in this problem. An additional condition is

$$R_{\ell 1}(s,0) \text{ continuous in } s .\tag{51}$$

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To solve the modified Eqs. (5) and (6) we first define the quantity

$$\psi(t) \;=\; \frac{G_2(t) - \frac{\alpha}{2} F_2(t)}{G_2(0) - \frac{\alpha}{2} F_2(0)} \;. \tag{52}$$

Adding Eqs. (49) we may obtain $[G_1(t) - (\alpha/2)F_1(t)]$ in terms of $\psi(t)$. Using these various relations in Eqs. (48), (50) and (51) we obtain the nonlinear differential equation for $\psi(t)$:

$$\psi + \lambda \,\frac{\alpha\rho_o}{2}\, e^{-at}\, \psi^{1-1/\lambda} \;=\; \frac{\beta_2}{2}\, e^{\beta_2 t/2} \;, \tag{53}$$

where

$$a \;=\; \frac{1}{2}(\alpha\rho_o + 2\beta_1 - \beta_2/\lambda) \;, \quad \psi(0) \;=\; 1 \;. \tag{54}$$

To compare the results of this problem to that of the more realistic problem considered earlier in this section we consider the plane $x = -L$ where

$$\alpha\rho_1(-L, \tau + L/c) \;=\; -\beta_1 + \frac{1}{\lambda}\, \psi^{-1+1/\lambda} \left\{ \beta_2\, e^{\beta_2 \tau/2} - (\beta_2 - \lambda\beta_1)\psi \right\}$$

$$\cdot \left\{ \psi^{1/\lambda} - \frac{\alpha\rho_o}{\alpha\rho_o + \beta_1}\, e^{-a\tau}\, (1 - G_1^{-1}) \right\}^{-1} \;. \tag{55}$$

$G_1 = e^{(\alpha\rho_o + \beta_1)L/c}$ and $\tau = t - L/c \geq 0$. Examinations of Eq. (53) both analytically and with the aid of a computer show that $\psi(t)$ drops very sharply — like $\exp(-\lambda g t)$ — from its initial value until it reaches a minimum at $t_1 \cong 30\,(\lambda g)^{-1}$. It increases gradually from that point onward. The backscattered photon density ρ_1 exhibits the expected pulse-like character. It rises to a maximum at a few times $(\lambda g)^{-1}$ earlier than t_1. The maximum ranged between $3\rho_o$ and $150\rho_o$ for the parameters considered, namely, $10 \text{ cm} \leq L \leq 100 \text{ cm}$ and $10 \leq \lambda \leq 150$.

It is our intention to complete the analysis of the pure boundary-value problem during the remainder of this contract.
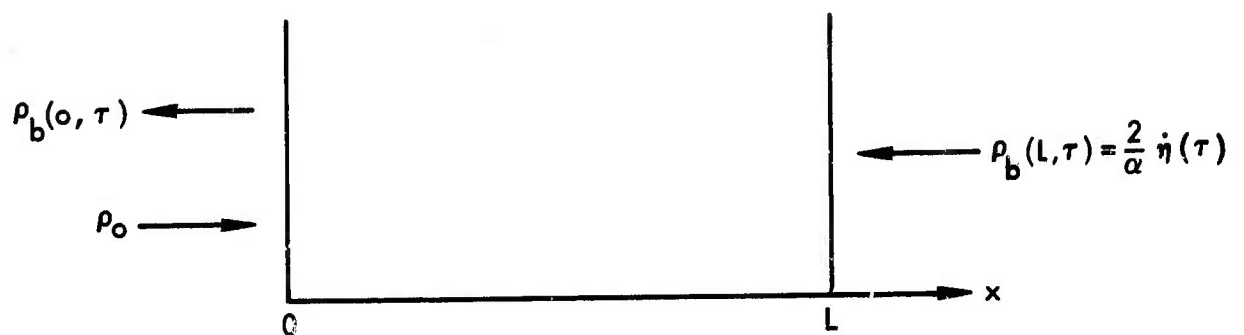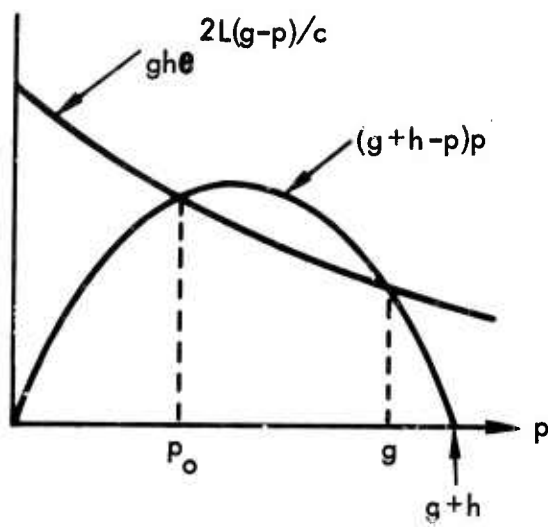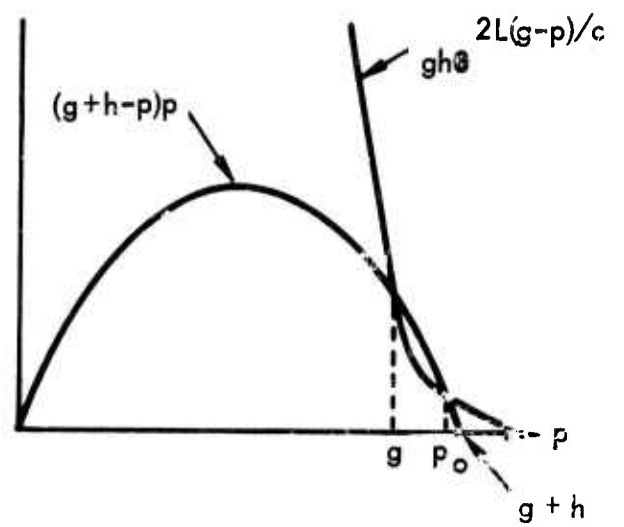
Figure 1. A Raman amplifier of length L, laser light — photon density ρ_o — is incident from the left at $x = 0$. The signal — light at the first Stokes frequency with a photon density $\rho_b(L,t)$ — is incident from the right at $x = L$. The amplified pulse — photon density $\rho_b(0,t)$ — is emitted at $x = 0$.

Figures 2. Determination of p_o from the intersection of $(g + h)p - p^2$ and $gh \exp[g - p)/c]$. If $2L/c < t_o = h^{-1} - g^{-1}$ then $0 < p_o < g$ as shown in Fig. 2a, whereas if $2L/c < t_o$ then $g < p_o < g + h$ as shown in Fig. 2b.
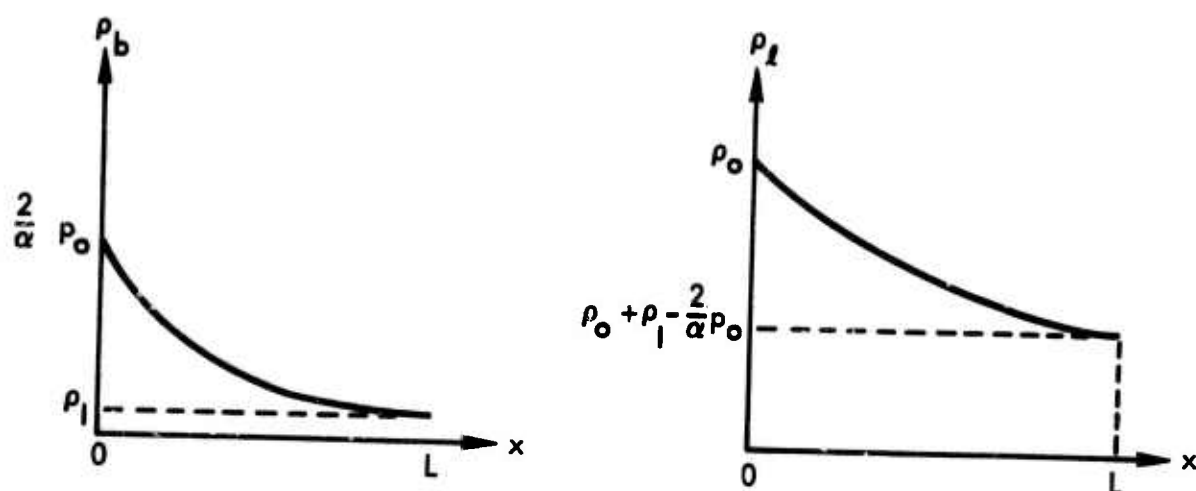
Figure 3. The photon density within the amplifier
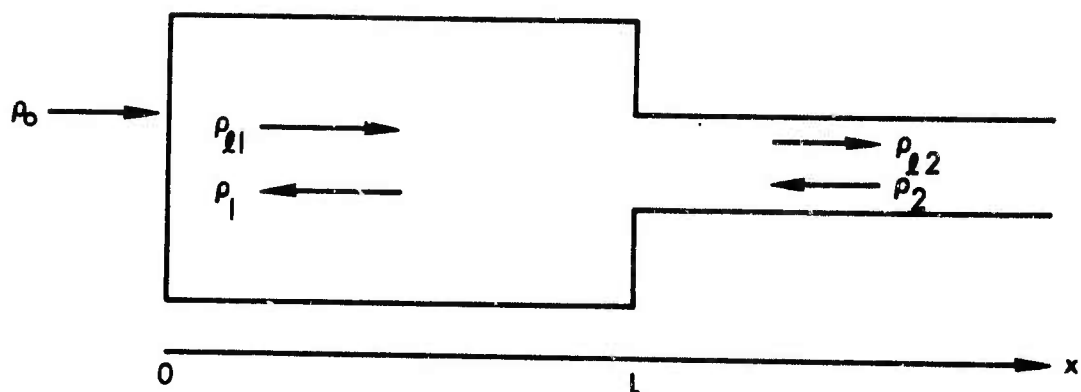in the limit $t \to \infty$.

Figure 4.   The Raman pulse generator.   A Raman active medium occupies the space $x > 0$.   Laser light — photon density ρ_0 — is incident on this medium from the right.   It propagates from $x = 0$ to $x = L$ with a constant cross-sectional area.   At $x = L$ self focusing occurs and the area of the beam decreases by a factor of $(1/\lambda) \ll 1$.   The laser and Raman photon densities are $\rho_{\ell 1}$ and ρ_1 respectively for $0 < x < L$, and $\rho_{\ell 2}$ and ρ_2 for $x > L$.

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13. ABSTRACT

Two nonlinear propagation effects which limit the transmission of intense laser radiation through the atmosphere are discussed, namely, self-defocusing due to atmospheric heating, and the stimulated Raman effect. The self-defocusing studies are restricted, in this report, to the heating mechanisms, and in particular to the theory of the very far wings of atmospheric absorption lines, beyond the domain of conventional pressure broadening theories. Specifically, in order to understand the apparent dominance of H_2O absorptivity in the atmosphere at the 10μ window, the very far wing collision broadening of the rotational spectrum of polar molecules is investigated. First, the classical Debye theory of dielectric absorptivity is extended to account for higher frequencies and finite collisional time duration. It is then demonstrated that this theory is inadequate to explain the dominant role of $H_2O - H_2O$ collisions observed in recent experiments at 10μ with $H_2O - N_2$ mixtures, and it is found necessary to introduce a new mechanism: a hindered rotation, or librational motion, arising from the angular dependence of the strong dipole-dipole interaction. Preliminary calculations indicate that this mechanism is promising. With regard to the Raman effect, a previously developed theory of stimulated Raman propagation is applied to describe a Raman amplifier and also to explain recent observations of very short intense pulses of Raman backscattered light.

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